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Facility Investigation (RFI) Guidance
Volume 3. Air and Surface Water Releases

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This document, which is presented in four volumes, is intended to assist Regional and State personnel in exercising the discretion conferred by regulation in developing requirements for the conduct of RCRA Facility Investigations, pursuant to 40 CFR 264. Conformance with this guidance is expected to result in the development of RFIs that meet the regulatory standard of adequately detecting and characterizing the nature and extent of releases. This document is not a regulation and should not be used as such. Regional and State personnel must exercise their discretion in using this guidance document as well as other relevant information in determining whether an RFI meets the regulatory standard.

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RCRA FACILITY INVESTIGATION (RFI) GUIDANCE

VOLUME III OF IV

AIR AND SURFACE WATER RELEASES

EPA 530/SW-87-001C

DRAFT

JULY 1987

WASTE MANAGEMENT DIVISION
OFFICE OF SOLID WASTE
U.S. ENVIRONMENTAL PROTECTION AGENCY

REPRODUCED BY
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ABSTRACT

On November 8, 1984, Congress enacted the Hazardous and Solid Waste Amendments (HSWA) to RCRA. Among the most significant provisions of HSWA are §3004(u), which requires corrective action for releases of hazardous waste or constituents from solid waste management units at hazardous waste treatment, storage and disposal facilities seeking final RCRA permits; and §3004(v), which compels corrective action for releases that have migrated beyond the facility property boundary. EPA will be promulgating rules to implement the corrective action provisions of HSWA, including requirements for release investigations and corrective measures.

This document, which is presented in four volumes, provides guidance to the owner or operator of hazardous waste management facilities as to the conduct of the second phase of the RCRA Corrective Action Program, the RCRA Facility Investigation (RFI). Instruction is provided for the development and performance of an investigation based on determinations made by the regulatory agency as expressed in the schedule of a permit or in an enforcement order issued under HSWA§3008(h). The purpose of the RFI is to obtain information to fully characterize the nature and extent of releases of hazardous waste or constituents. This information will be used to determine whether interim corrective measures or a Corrective Measures Study will be necessary.

DISCLAIMER

This Draft Report was prepared for the U.S. Environmental Protection Agency by the NUS Corporation, Waste Management Services Group, Gaithersburg, MD 20878, in fulfillment of Contract No. 68-01-7310, Work Assignment No. 5, and is based on previous work performed by Alliance Technologies, Inc., under Contract No. 68-01-6871. The opinions, findings, and conclusions expressed herein are those of the authors and not necessarily those of the U.S. Environmental Protection Agency or the cooperating agencies. Mention of company or product names is not to be considered an endorsement by the U.S. Environmental Protection Agency.

This document is intended to assist Regional and State personnel in exercising the discretion conferred by regulation in developing requirements for the conduct of RCRA Facility Investigations (RFIs) pursuant to 40 CFR 264. Conformance with this guidance is expected to result in the development of RFIs that meet the regulatory standard of adequately detecting and characterizing the nature and extent of releases. However, EPA will not necessarily limit acceptable RFIs to those that comport with the guidance set forth herein. This document is not a regulation (i.e., it does not establish a standard of conduct which has the force of law) and should not be used as such. Regional and State personnel must exercise their discretion in using this guidance document as well as other relevant information in determining whether an RFI meets the regulatory standard.

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RCRA FACILITY INVESTIATION (RFI) GUIDANCE

VOLUME III

AIR AND SURFACE WATER RELEASES

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LIST OF ACRONYMS

AA - Atomic Absorption
AI - Soil Adsorption Isotherm Test
ASCS - Agricultural Stabilization and Conservation Service
ASTM - American Society for Testing and Materials
BCF - Bioconcentration Factor
BOD - Biological Oxygen Demand
CAG - EPA Carcinogen Assessment Group
CPF - Carcinogen Potency Factor
CBI - Confidential Business Information
CEC - Cation Exchange Capacity
CERCLA - Comprehensive Environmental Response, Compensation, and Lability Act
CFR - Code of Federal Regulations
CIR - Color Infrared
CM - Corrective Measures
CMI - Corrective Measures Implementation
CMS - Corrective Measures Study
COD - Chemical Oxygen Demand
COLIWASA - Composite Liquid Waste Sampler
DNPH - Dinitrophenyl Hydrazine
DO - Dissolved Oxygen
DOT - Department of Transportation
ECD - Electron Capture Detector
EM - Electromagnetic
EP - Extraction Procedure
EPA - Environmental Protection Agency
FEMA - Federal Emergency Management Agency
FID - Flame Ionization Detector
Foc - Fraction organic carbon in soil
FWS - U.S. Fish and Wildlife Service
GC - Gas Chromatography
GC/MS - Gas Chromatography/Mass Spectroscopy
GPR - Ground Penetrating Radar
HEA - Health and Environmental Assessment
HEEP - Health and Environmental Effects Profile
HPLC - High Pressure Liquid Chromatography
HSWA - Hazardous and Solid Waste Amendments (to RCRA)
HWM - Hazardous Waste Management
ICP - Inductively Coupled (Argon) Plasma
ID - Infrared Detector
Kd - Soil/Water Partition Coefficient
Koc - Organic Carbon Absorption Coefficient
Kow - Octanol/Water Partition Coefficient
LEL - Lower Explosive Limit
MCL - Maximum Contaminant Level
MM5 - Modified Method 5
MS/MS - Mass Spectroscopy/Mass Spectroscopy
NFIP - National Flood Insurance Program
NIOSH - National Institute for Occupational Safety and Health
NPDES - National Pollutant Discharge Elimination System
OSHA - Occupational Safety and Health Administration

LIST OF ACRONYMS (Continued)

OVA - Organic Vapor Analyzer
PID - Photo Ionization Detector
pKa - Acid Dissociation Constant
ppb - parts per billion
ppm - parts per million
PUF - Polyurethane Foam
PVC - Polyvinyl Chloride
QA/QC - Quality Assurance/Quality Control
RCRA - Resource Conservation and Recovery Act
RFA - RCRA Facility Assessment
RfD - Reference Dose
RFI - RCRA Facility Investigation
RMCL - Recommended Maximum Contaminant Level
RSD - Risk Specific Dose
SASS - Source Assessment Sampling System
SCBA - Self Contained Breathing Apparatus
SCS - Soil Conservation Service
SOP - Standard Operating Procedure
SWMU - Solid Waste Management Unit
TCLP - Toxicity Characteristic Leaching Procedure
TEGD - Technical Enforcement Guidance Document (EPA, 1986)
TOC - Total Organic Carbon
TOT - Time of travel
TOX - Total Organic Halogen
USGS - United States Geologic Survey
USLE - Universal Soil Loss Equation
UV - Ultraviolet
VOST - Volatile Organic Sampling Train
VSP - Verticle Seismic Profiling
WQC - Water Quality Criteria

SECTION 12

AIR

12.1 Overview

The objective of an investigation of a release to air is to characterize the nature, extent, and rate of migration of the release of hazardous waste or constituents to that medium. This is done by characterizing long-term ambient air concentrations (commensurate with the long-term exposures which are the basis for the health and environmental criteria presented in Section 8) associated with unit releases of hazardous wastes or constituents to air. This section provides:

- A recommended strategy for characterizing releases to air, which includes characterization of the source and the environmental setting of the release, and conducting a monitoring and/or modeling program which will characterize the release itself;
- Recommendations for data organization and presentation;
- Field methods which may be used in the investigation; and
- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all instances; it identifies possible information necessary to perform release characterizations and methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information for release characterization. This list is not a list of requirements for all releases to air. Some release investigations will involve the collection of only a subset of the items listed, while other releases may involve the collection of additional data.

Case studies 14 and 15 in Volume IV (Case Study Examples) illustrate several of the air investigation concepts discussed in this section.

12.2 Approach for Characterizing Releases to Air

12.2.1 General Approach

The intent of the air release investigation is to determine actual or potential effects on off-site receptors. This differs from the other media discussed in this Guidance. During the health and environmental assessment process for the air medium (see Section 8), the decision as to whether interim corrective measures or a Corrective Measures Study will be necessary is based on actual or potential effects on off-site receptors, and is not (as with the other media), based on potential effects beyond the boundary of the waste management area. This general approach is detailed in the sections below.

12.2.1.1 Information Collection/Air Monitoring

Characterization of releases from waste management units to air may be approached in a tiered or phased fashion as described in Section 3. The key elements to this approach are shown in Table 12-1. An overview of the release characterization strategy for air is illustrated in Figures 12-1 through 12-5.

Two major elements can be derived from this strategy:

- Collection and review of data to be used for characterization of the source of the air release and the environmental setting for this source. Source characteristics will include obtaining information on the unit operating conditions and configuration, and may entail a sampling and analytical effort to characterize the waste material in the unit or the incoming waste streams.

- Development and implementation of monitoring and/or modeling procedures to be used for characterization of the release (from a unit or contaminated soil) itself. Utilizing a phased approach, the air release is

Table 12-1

Recommended Strategy for Characterizing Releases to Air*

INITIAL PHASE

1. Collect and review preliminary information for use in formulating monitoring procedures:

   - Characterization of the Contaminant Source
     Waste Characterization
     Unit Characterization

   - Characterization of the Environmental Setting
     Climate (especially wind patterns which may require an onsite meteorological monitoring survey)
     Soil
     Terrain
     Receptors

   - Review of Existing Air Monitoring Results

   - Determination of "Reasonable Worst Case" exposure period over a 90 day period at point of evaluation

2. Identify and collect additional information necessary to characterize release:

   - Spatial extent of release
   - Release constituents present and concentration levels
   - Inter-media transport
   - Conceptual model of release

3. Develop monitoring procedures:

   - Conduct screening sampling
     Verify existence of release
     Emphasis on near-source sampling
     Provide information to finalize monitoring program design
   - Meteorological monitoring
   - Determining constituents of concern/indicator parameters
   - Sampling approach selection
   - Sampling schedule
   - Monitor placement
   - Analytical Methods
   - QA/QC protocols

4. Conduct initial monitoring phase:

   - Evaluate upwind (background) and air quality levels downwind of the source

Table 12-1 (Continued)

Recommended Strategy for Characterizing Releases to Air

- If practical, conduct air monitoring at or near actual offsite receptor locations in order to characterize exposures at these points of evaluation
- Collect samples and complete field analyses
- Analyze samples for selected constituents and parameters

5. Collect, evaluate and report results:

   - Account for source and meteorological data variability during monitoring program
   - Evaluate long-term representativeness of air monitoring data
   - Apply emission/dispersion models as appropriate to aid in data interpretation and to estimate air constituent concentrations levels at actual points of offsite exposure
   - EPA as well as owner or operator to independently compare monitoring/modeling results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures
   - Determine completeness and adequacy of collected data
   - Summarize and present data in appropriate format
   - Determine if monitoring program objectives were met
   - Determine if monitoring locations, constituents and frequency were adequate to characterize release

SUBSEQUENT PHASES (If necessary)

1. Identify additional information necessary to characterize release:

   - May be required if air concentration levels are of concern based on health and environmental assessment and more refined concentration estimates (e.g., larger monitoring data base or additional monitoring stations at actual offsite receptor locations) are needed to characterize the release
   - May be required after corrective measures have been identified and implemented to evaluate air concentration trends

2. Expand initial monitoring as necessary:

   - Expand air monitoring network as necessary (e.g., downwind monitoring at locations further downwind may be warranted at complex terrain sites for which modeling results would have a high degree of uncertainty or at actual offsite points of evaluation if practical)

3. Conduct subsequent monitoring phases:

   - Perform expanded monitoring of area
   - Analyze samples for selected constituents and parameters

Table 12-1 (Continued)

Recommended Strategy for Characterizing Releases to Air

4. Collect evaluate and report results/identify additional information necessary to characterize release:

    - Account for source and meteorological data variability during monitoring program
    - Evaluate long-term representativeness of air monitoring data
    - Apply emission/dispersion models as appropriate to aid in data evaluation and to provide concentration estimates at actual offsite receptor locations as input to health and environmental assessment
    - EPA as well as owner or operator to independently compare monitoring results to health and environmental criteria and identify respond to emergency situations and identify priority situations that may warrant interim corrective measures
    - Determine completeness and adequacy of collected data
    - Summarize and present data in appropriate format
    - Determine if monitoring program objectives were met
    - Determine if monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)
    - Identify additional information needs, if necessary
    - Determine need to expand monitoring system
    - Evaluate potential role of inter-media transport

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* The potential for inter-media transport of contamination should be evaluated continually throughout the investigation.

FIGURE 12-
RELEASE CHARACTERIZATION STRATEGY FOR AIR-OVERVIEW

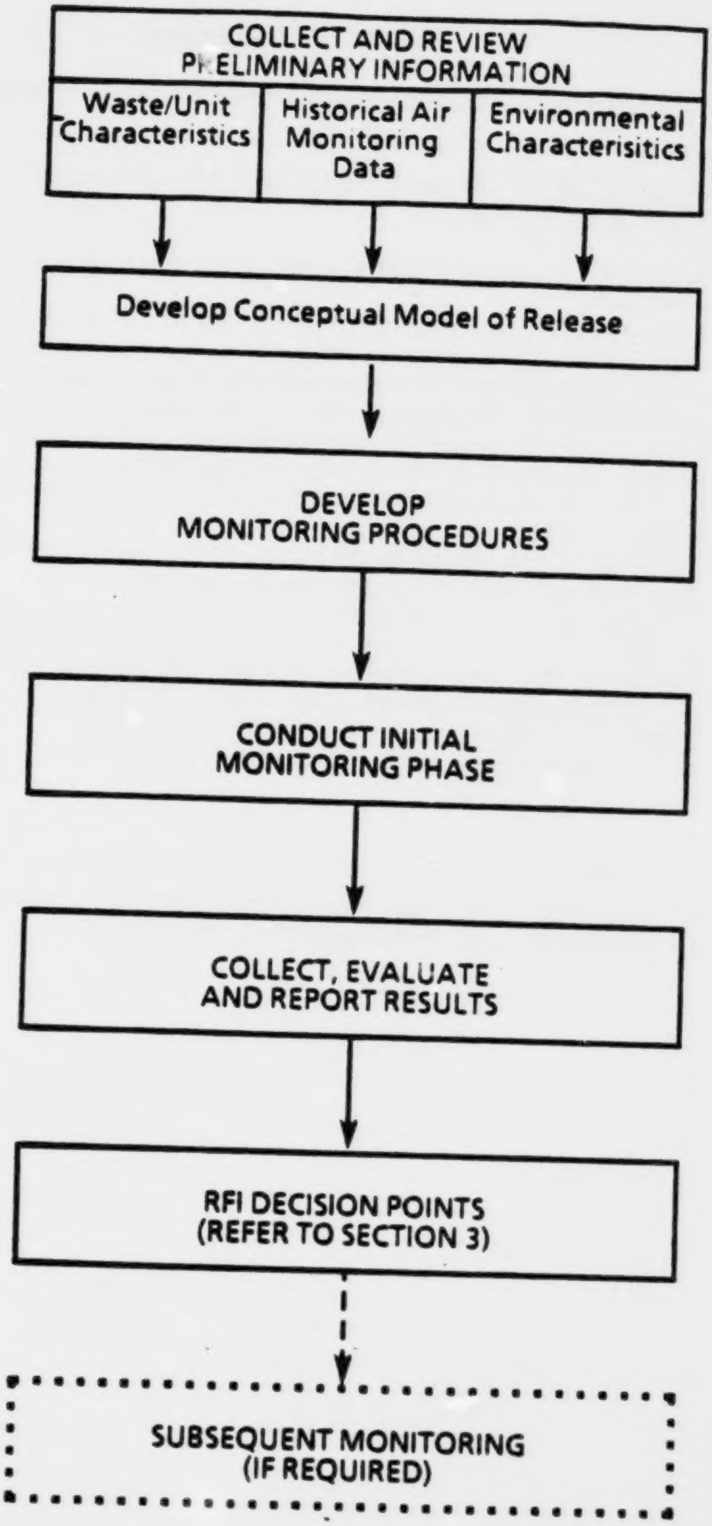
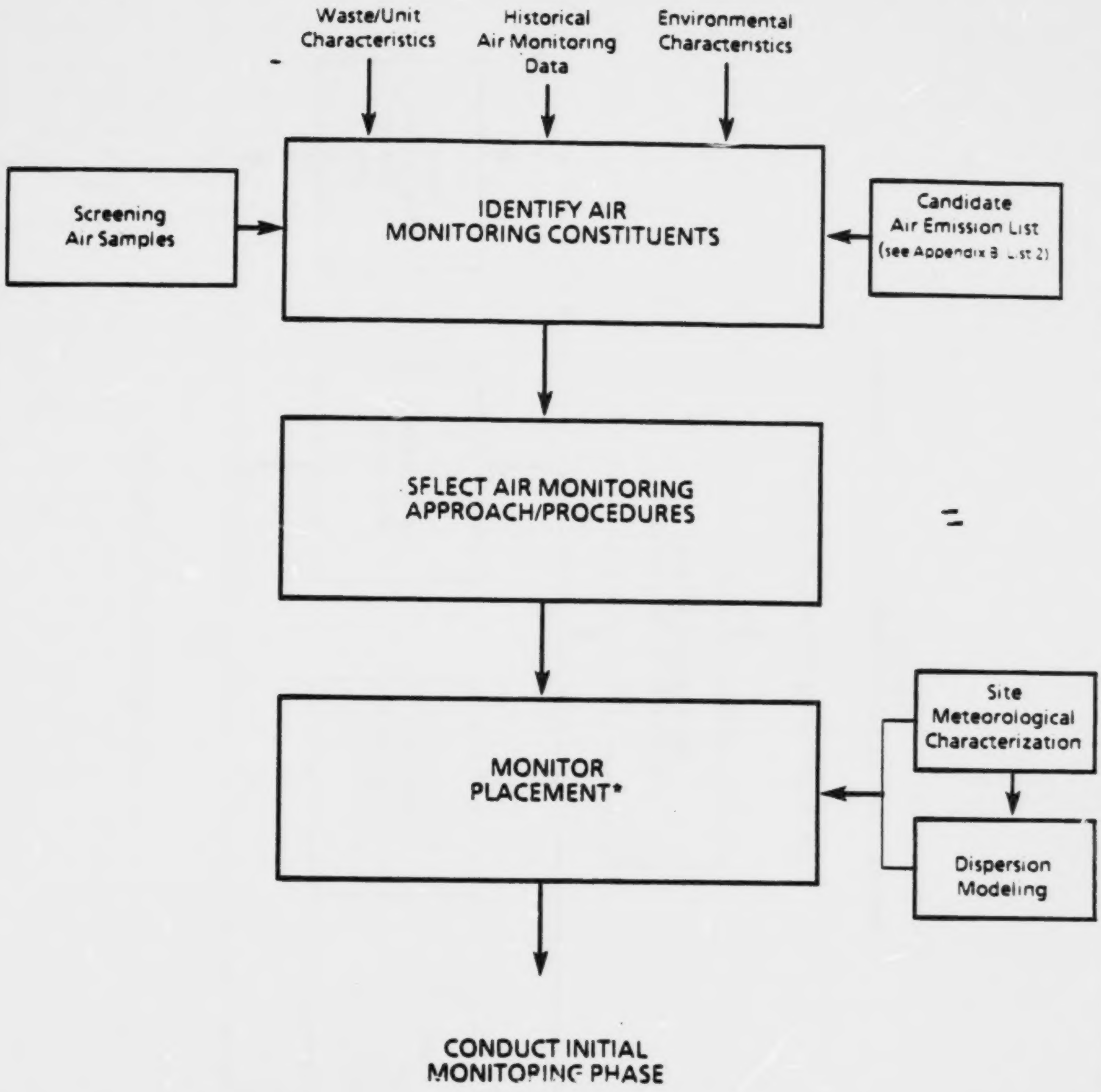
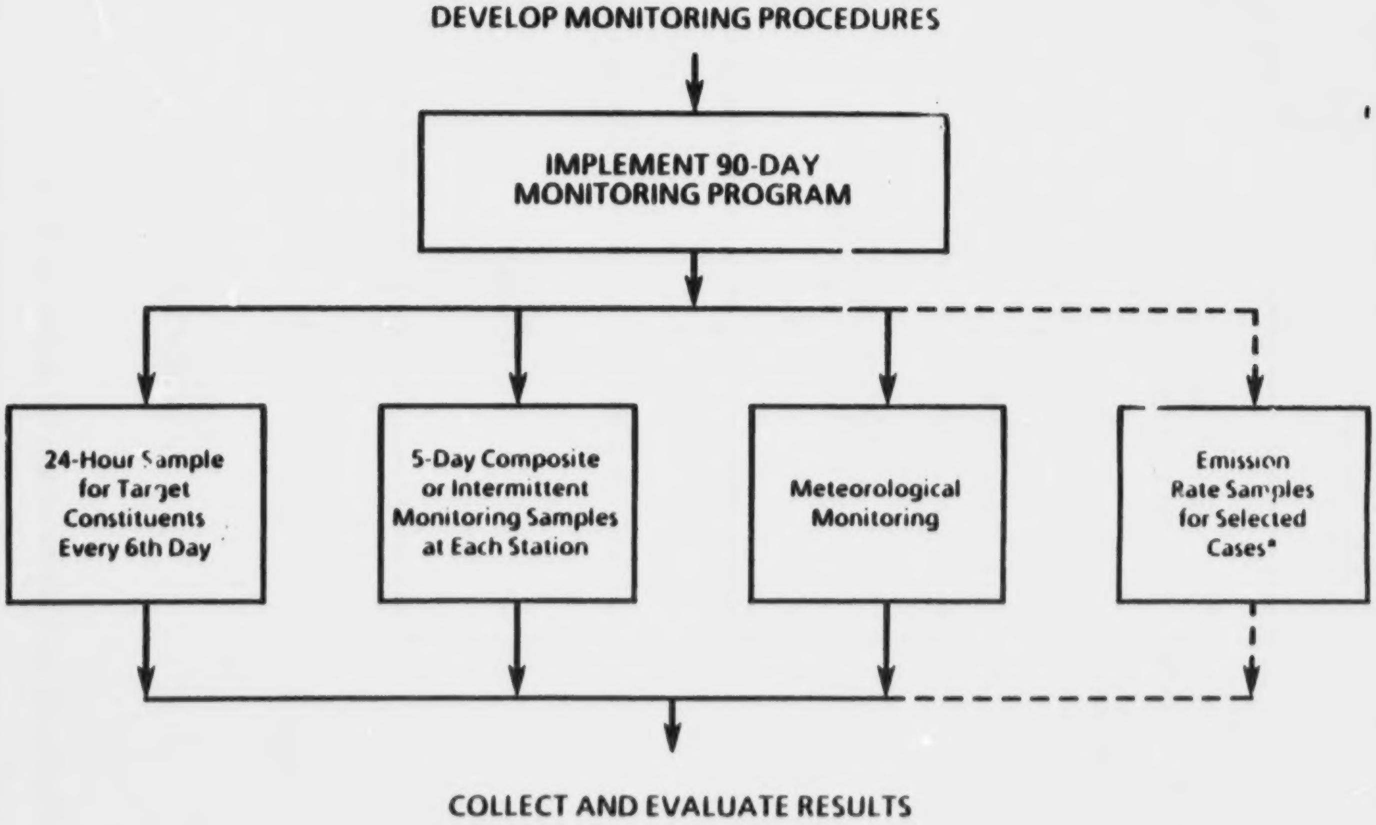

COLLECT AND REVIEW PRELIMINARY INFORMATION
Waste/Unit Characteristics
Historical Air Monitoring Data
Environmental Characterisitics
Develop Conceptual Model of Release
DEVELOP MONITORING PROCEDURES
CONDUCT INITIAL MONITORING PHASE
COLLECT, EVALUATE AND REPORT RESULTS
RFI DECISION POINTS (REFER TO SECTION 3)
SUBSEQUENT MONITORING (IF REQUIRED)

FIGURE 12-2
DEVELOP MONITORING PROCEDURES - OVERVIEW


Waste/Unit Characteristics
Historical Air Monitoring Data
Environmental Characteristics
Screening Air Samples
IDENTIFY AIR MONITORING CONSTITUENTS
Candidate Air Emission List (see Appendix B List 2)
SELECT AIR MONITORING APPROACH/PROCEDURES
Site Meteorological Characterization
MONITOR PLACEMENT*
Dispersion Modeling
CONDUCT INITIAL MONITORING PHASE

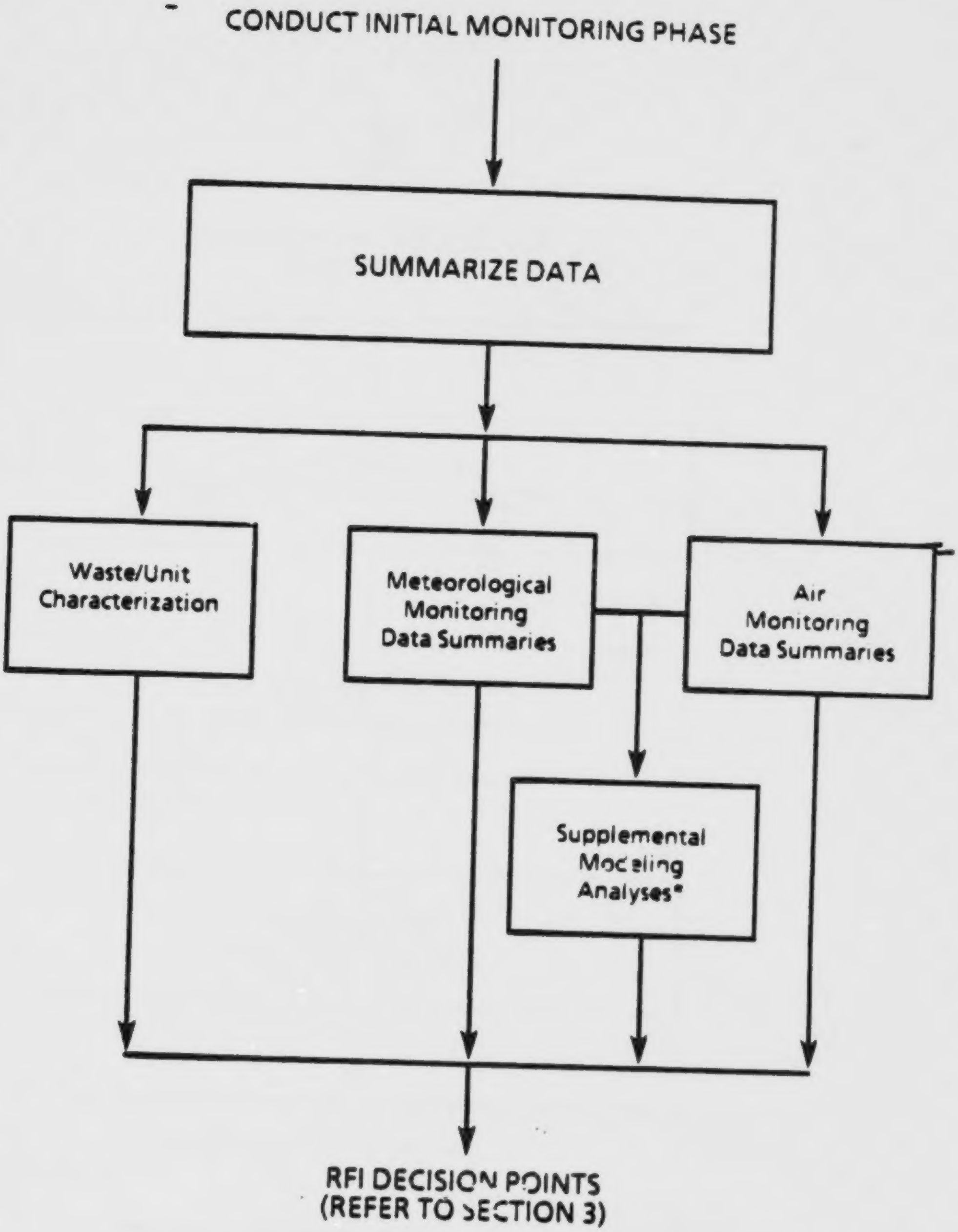
*
- At facility to increase potential for release detection
- At actual receptors beyond the facility property boundary to support health and environmental assessment (if practical)

FIGURE 12-3
CONDUCT INITIAL MONITORING PHASE - OVERVIEW


DEVELOP MONITORING PROCEDURES
IMPLEMENT 90-DAY MONITORING PROGRAM
24-Hour Sample for Target Constituents Every 6th Day
5-Day Composite or Intermittent Monitoring Samples at Each Station
Meteorological Monitoring
Emission Rate Samples for Selected Cases*
COLLECT AND EVALUATE RESULTS

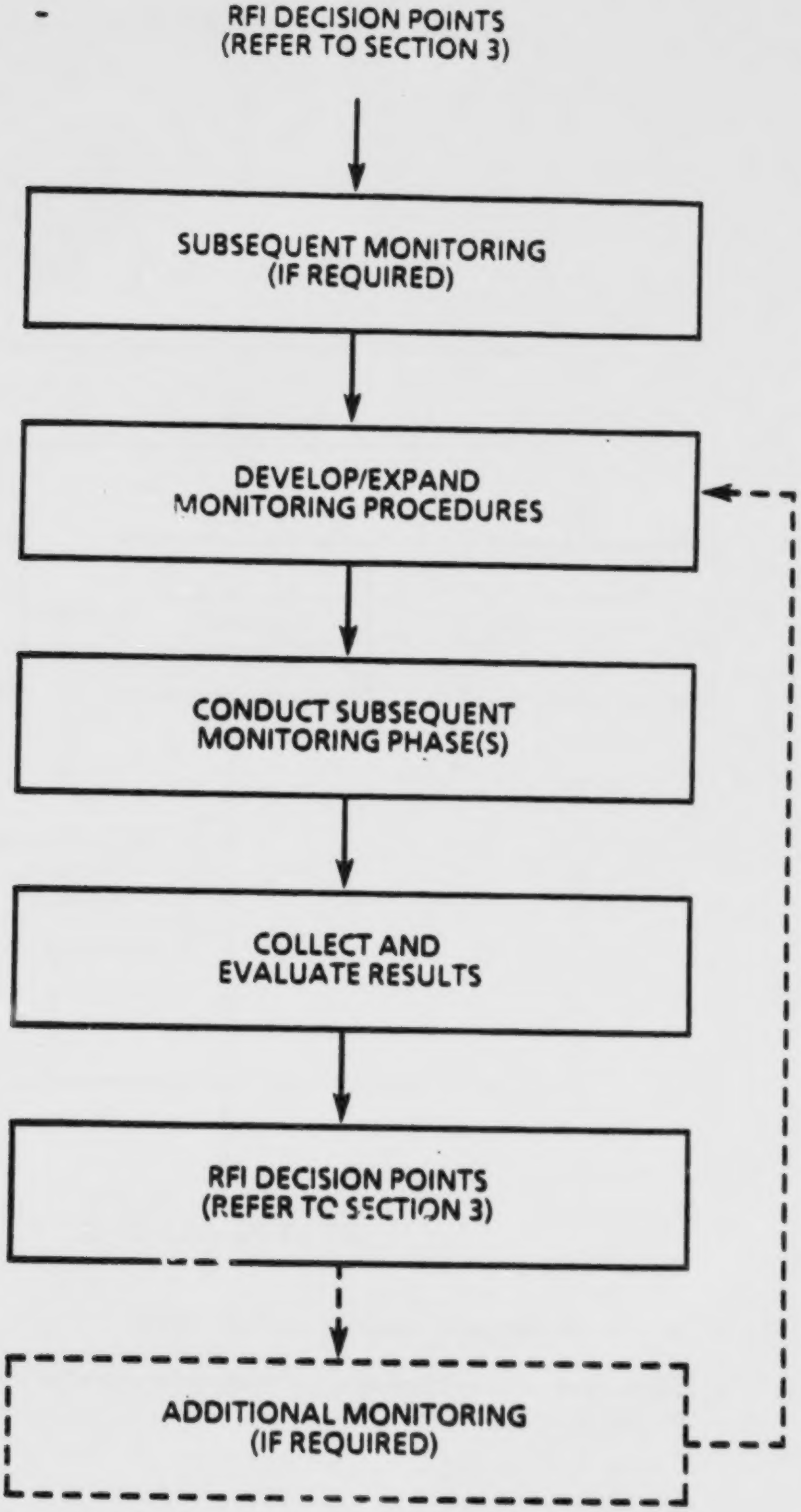
* To be implemented if ambient air contamination is suspected to be less than monitoring detection levels and waste characterization data not sufficient for application of air emission release rate models

FIGURE 12-4
COLLECT AND EVALUATE RESULTS - OVERVIEW


CONDUCT INITIAL MONITORING PHASE
SUMMARIZE DATA
Waste/Unit Characterization
Meteorological Monitoring Data Summaries
Air Monitoring Data Summaries
Supplemental Modeling Analyses*
RFI DECISION POINTS (REFER TO SECTION 3)

*
- To evaluate representatives of air monitoring data
- To estimate concentrations at actual receptor locations beyond the facility property boundary (as necessary)

FIGURE 12-5
SUBSEQUENT MONITORING - OVERVIEW


RFI DECISION POINTS (REFER TO SECTION 3)
SUBSEQUENT MONITORING (IF REQUIRED)
DEVELOP/EXPAND MONITORING PROCEDURES
CONDUCT SUBSEQUENT MONITORING PHASE(S)
COLLECT AND EVALUATE RESULTS
RFI DECISION POINTS (REFER TO SECTION 3)
ADDITIONAL MONITORING (IF REQUIRED)

characterized in terms of the types and amounts of hazardous constituents being emitted, leading to a determination of actual or potential exposure to offsite receptors. This may involve ambient monitoring (i.e., monitoring concentrations at locations away from the source) and/or emission monitoring (i.e., monitoring at a source to determine emission rates), coupled with dispersion modeling. A phased approach may not always be necessary to achieve adequate release characterization.

This strategy provides an acceptable technical approach to characterize the nature and extent of air releases from units. The collection and review of information for characterization of the contaminant source and the environmental setting is the primary basis for development of monitoring procedures used to characterize air emissions. These input data should be compiled from available sources. The air pathway data collection effort should also be coordinated, as appropriate, with similar efforts for other media investigations. Tasks for implementing the release characterization strategy for releases to air are summarized in Table 12-2.

An important aspect of the environmental characterization process is the need to identify site-specific wind patterns as a basis for specifying the station locations for the air monitoring network. This will generally require an onsite meteorological monitoring survey prior to completing the design of the air monitoring program.

The meteorological monitoring survey should be conducted for at least one month, or longer if necessary (especially at complex terrain and coastal locations), to define diurnal and seasonal wind patterns expected during the air monitoring phase of the RFI. The limited onsite data should be compared to representative, long-term meteorological data to account for expected seasonal variations at the site. Representativeness of the onsite monitors can be evaluated by comparing short-term onsite versus long-term offsite wind distributions (wind roses), stability frequency tables, and dispersion patterns based on modeling results (assuming an arbitrary source emission rate). An onsite meteorological monitoring survey may not be necessary for inland flat terrain site for which regional National Weather Service station data representative of local site conditions are available.

Table 12-2
Release Characterization Tasks for Air

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs
1. Waste/Unit Characterization		
- Identification of waste constituents	- See Section 3, 7 and Volume I, Appendix B List 2	- Listing of potential release constituents
- Prioritization of air emission constituents	- Waste sampling and characterization	- Listing of target air emission constituents for monitoring
- Identification of unit characteristics which may promote an air release	- See Section 7	- Description of the unit
2. Environmental Setting Characterization		
- Definition of climate	- Climate summaries for regional National Weather Service stations (may require onsite meteorological monitoring survey)	- Wind roses and statistical tabulations for parameters of interest
- Definition of site-specific meteorological conditions	- Onsite meteorological monitoring concurrent with air monitoring	- Wind roses and tabulations for parameters of interest
- Definition of soil conditions to characterize emission potential for particulate emissions and for certain units (e.g., landfills and land treatment) for gaseous emissions	- See Section 9	- Soil physical properties (e.g., porosity, organic matter content)
- Definition of site-specific terrain	- See Section 7, 9 and Appendix A (Volume 1) of RFI and recent aerial photographs and U.S. Geolgoical Survey maps	- Topographic map of site area
- Identification of potential air-pathway receptors	- Census data, area surveys, recent aerial photographs and U.S. Geological Survey topographic maps	- Map with identification of nearby populations and buildings
3. Release Characterization		
- Identification of "Reasonable Worst Case" conditions	- Wind patterns and/or emission/dispersion modeling	- Monthly seasonal wind roses and/or table of predicted concentrations as a function of downwind distances and wind/stability conditions
- Screening evaluation of air release to finalize air monitoring program design and select target constituents of concern	- Limited source/near-source sampling	- Listing of concentration levels
- Characterization of target constituents	- Upwind/downwind air monitoring, or (for certain situations) source emission rate monitoring/dispersion modeling	- Tables of concentrations. Detailed assessment of extent and magnitude of air releases

Development of monitoring procedures generally includes the collection of meteorological data concurrent with air quality measurements. The meteorological data are needed during the air monitoring program to characterize emission potential and atmospheric dispersion conditions. This information is also used to evaluate source/receptor relationships and to interpret the air monitoring data.

Development of monitoring procedures should address selection of target air emission constituents. One acceptable approach is to monitor for all Appendix VIII potential air emission constituents (See Appendix B, List 2) applicable to the unit or release of concern. An alternative approach is to use unit- and waste-specific information to identify constituents that are expected to be present, thus reducing the list of target monitoring constituents (See Section 3.6).

Development of monitoring procedures should also include selection of appropriate field and analytical methods for conducting the air monitoring program. Candidate methods and criteria for monitoring program design (e.g., relevant to sampling schedule and monitor placement) should be limited to standard published protocols (such as those available from EPA, NIOSH, and ASTM). Selection of appropriate methods will be dependent on site and unit-specific conditions.

The air monitoring program will generally consist of several phases as follows:

- Screening sampling to verify the presence of a suspected release (in those cases where release verification is appropriate), to prioritize sources (based on emission potential as determined by obtaining air samples at or near the source) at multiple-unit facilities, and to obtain information to aid in design of the air monitoring program;

- Initial monitoring (air monitoring should be conducted for a 90-day period) to characterize air concentrations at actual offsite receptor locations as input to the health and environmental assessment. This will generally involve air monitoring stations at the facility (to maximize the potential for detection of the release) and at actual offsite receptor locations (if practical), or application of dispersion models to estimate offsite concentration levels at receptor locations; and

- Subsequent monitoring, if needed, to better define the magnitude and extent of the release to air or, in certain cases, to evaluate the air concentration levels subsequent to the implementation of corrective measures. Subsequent monitoring will be necessary if results of initial monitoring and modeling do not provide an adequate basis for estimating long-term exposures at actual offsite receptor locations. For example, subsequent monitoring would be necessary if the initial monitoring phase was not representative of long-term exposure conditions.

All phases may not be needed for each investigation depending on the site-specific air monitoring data available and the nature and magnitude of the release.

A limited sampling program may be necessary for screening purposes to finalize design of the air monitoring program. The objective of this screening sampling will be to verify a suspected release, if appropriate, and to further assist in identificating and quantifying of release constituents of concern. Screening sampling at each unit for a multiple-unit facility can be used to prioritize release sources. Therefore, the emphasis during this screening will be on obtaining air samples near the source, or collecting a limited number of source emission samples. The availability of air monitoring data or units with a limited set of air emission constituents may preclude the need for screening sampling during the RFI process.

An initial air monitoring program should be conducted, as necessary, to characterize the magnitude and distribution of air concentration levels for the target constituents selected. Subsequent monitoring may also be necessary to more thoroughly evaluate concentration levels at offsite receptors.

The basic approach for the initial air monitoring will consist of collection of ambient air samples for four target zones: the first zone located upwind of the source to define background contamination levels; the second zone located downwind at the unit boundary; the third zone located downwind at the facility property boundary to maximize the potential for release detection; and a fourth zone offsite, as practical, to determine concentrations at actual offsite receptors for input into the health and environmental assessment. Offsite air monitoring may not always be practical due to various problems (e.g., vandalism, public tampering with equipment, public relations and legal access problems). Dispersion modeling can be used to estimate offsite concentrations if monitoring data are not available for the actual receptor locations of interest. Multiple monitoring stations will generally be required for each of the four target zones.

The location of air monitors within each zone should be based on site-specific diurnal and seasonal wind patterns appropriate for the monitoring period. The objective of the monitoring network should be to provide adequate coverage for primary air flowpaths for each of the zones enumerated above.

As concentration measurements or estimates for offsite receptor locations become available, both within and at the conclusion of discrete investigation phases, they should be reported to the regulatory agency as directed. The regulatory agency will compare the concentrations with applicable health and environmental criteria to determine the need for (1) interim corrective measures; and (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the data with respect to adequacy and completeness to determine the need for any additional characterization efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are supplied in Section 8. A flow diagram illustrating RFI Decision Points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is advised and follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

12.2.1.2 Emission/Dispersion Modeling

Modeling can be an integral part of the release characterization for air. The major modeling applications can be summarized as follows:

- Emission models can be used in conjunction with screening sampling results to prioritize sources at a facility to support the design of an air monitoring program (e.g., to identify units that warrant placement of one or more air monitoring stations nearby);

- Dispersion models can be used to identify expected high concentration areas relative to actual offsite receptor locations which can be considered priority locations for air monitoring stations;

- Dispersion models, using available onsite or offsite historical meteorological data, can be used to identify the "reasonable worst case" 90-day period for conducting the air monitoring program;

- Dispersion models with concurrent meteorological monitoring data as input can be used to determine if the air monitoring was conducted during "reasonable worst case" conditions;

- Monitoring and/or emission rate data are available within the facility property boundary, dispersion models can be used to estimate concentrations at actual offsite receptor locations if monitoring data are not available for these locations; and

- Both emission and dispersion models can be used to estimate concentrations if analytical detection limits for ambient and emission rate (source) monitoring are greater than expected constituent concentrations.

Emission rate models can provide a screening test to support the design of an air monitoring program. These models can be used to identify potential major air emission sources at a facility (especially multiple unit-facilities). For this type of application, modeling results are used to compare routine long-term emissions from various units to prioritize the need for air monitoring at each unit. (For example, modeling results may indicate that 90 percent of the volatile organic compound emissions at a facility are attributable to surface impoundment units and only 10 percent to other sources. Therefore, emphasis should be on characterizing releases from the surface impoundments.) Emission rate modeling results are used on a comparative basis; absolute emission rates are not a primary objective of the assessment.

Atmospheric dispersion models can also be used to assist in designing an air monitoring program. Modeling results can be used to identify offsite areas of high concentration relative to actual receptor locations. High concentration areas which correspond to actual receptors are priority locations for air monitoring stations.

Dispersion models can also be used to provide seasonal dispersion "patterns" based on available representative historical meteorological data (either onsite or offsite). Comparison of seasonal dispersion patterns can be used to identify "reasonable worst case" 90-day period for monitoring. Dispersion patterns based on modeling results can similarly be used to evaluate the representativeness of the data collection period. Representativeness is determined by comparing the dispersion patterns for the air monitoring period with historic seasonal dispersion patterns.

Frequently, it may not be practical to place air monitoring stations at actual offsite receptor locations. However, it will be necessary to characterize concentrations at these locations to conduct a health and environmental assessment. In these cases, dispersion patterns based on modeling results can be used to extrapolate concentrations monitored at the facility property boundary to offsite receptor locations.

Modeling can also be used to estimate offsite concentrations if it is not feasible to collect air monitoring data at the facility property boundary. Source emission rate monitoring data may be collected for some situations if analytical detection limits for ambient monitoring are expected to be less than constituent concentrations. These emission rate monitoring data can be input into a dispersion model that can be used to estimate offsite concentrations.

The objective of the modeling applications discussed above involves the estimation of long-term (i.e., several months to years) concentration patterns. These long-term patterns do not have the variability associated with short-term (i.e., hours to days, such as a 24-hour event) emission rate and dispersion conditions.

Concentration patterns derived from models will primarily be used to estimate relatively high concentration areas. For such an application, it will not be necessary to calculate actual concentrations; instead, dispersion or dilution patterns are derived. Dispersion or dilution patterns illustrate the relative change in concentration as a function of distance and direction from the release source. As an example, dilution pattern results may indicate that the concentration at the nearest receptor is expected to be one half of the value at the facility property boundary. Therefore, if a 10 ug/m3 value was measured at the facility property boundary, a concentration of 5 ug/m3 would be expected at the nearest receptor.

Modeling applications are, however, limited by the amount, quality, and representativeness of the input data. Meteorological data are the key input for developing dispersion or dilution patterns. In addition, standard dispersion models are not considered to be accurate for most complex terrain applications (results can be off by greater than a factor of 10). Air emission release rate models require waste constituent information as key input. However, the spatial variation of wastes at some units may not be well known and, therefore, modeling may not be appropriate if adequate input data are not available.

The use of the Industrial Source Complex (ISC) Model is recommended for evaluating dispersion of hazardous air pollutants. Applicable ISC source types include stack, area, and volume sources. Concentration estimates can be based on times of as short as one hour and as long as annual average times. The model can be used for both flat and rolling terrain. The ISC model can also account for atmospheric deposition (i.e., inter-media transport to soil). The ISC Model, (see EPA 450/4-79-030) as well as alternative EPA-approved models (e.g., the UNAMAP series) is available through the NTIS.

Alternative dispersion models, including the use of simple screening models (e.g., EPA-model Point Plume, PTPLU) or hand calculation approaches are available for point sources located in flat terrains based on the following guidance:

Turner, D.B. 1969. Workbook of Atmospheric Dispersion Estimates. Public Health Service. Cincinnati, OH.

Guidance on application of the ISC model and other acceptable dispersion models, as well as on modeling for complex terrain sites is provided in the following documents:

U.S. EPA. July, 1986. Guidelines on Air Quality Models (Revised). EPA-450/2-78-027R. NTIS PB86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. October 1977. Guidelines for Air Quality Maintenance Planning and Analysis. Vol. 10 (Revised): Procedures for Evaluating Air Quality Impact of New Stationary Sources. EPA-450/4-77-001. NTIS PB274-087. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

Air emission release rate models, including models that are available for use on personal computers, are presented in the following reference:

U.S. EPA. 1987 Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF) - Air Emission Models - Draft Report. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Additional pertinent references include the following:

U.S. EPA. 1985. Compilation of Air Pollutant Emission Factors. EPA, AP-42. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. 1984. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage and Disposal Facilities. EPA 450/3-84-020. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. June, 1984. Evaluation of Air Emissions from Hazardous Waste Treatment, Storage and Disposal Facilities. EPA 600/2-85-1057. Office of Research and Development. Cincinnati, OH 45268.

U.S. EPA. February, 1985. Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites. EPA/600-18-85/002. Office of Health and Environmental Research. Washington, D.C. 20460.

For some applications, it can be assumed that all the volatile wastes handled will eventually be emitted to the air. This assumption is generally appropriate for volatile organic compounds placed in a disposal unit such as a surface impoundment. In these cases, the air emission rate can be assumed to be equivalent to the disposal rate and a emission rate model may not be required. This assumption is valid because of the long-term residence time for wastes in the disposal units. Frequently, a substantial portion of the volatile constituents will be released to the atmosphere within several days from open units such as surface impoundments. However, for more complex situations (e.g., storage or treatment units where total volatilization of the constituents is not expected), air emission models can be used to obtain a more refined long-term release rate.

Before proposing any models, the owner or operator is advised to consult with the regulatory agency.

12.2.2 Inter-media Transport

Subsurface gas migration, contaminated surface water and contaminated soil can all result in inter-media transport of contaminants to air. Subsurface gas can migrate to the land surface or be released to the atmosphere artificially from gas vents or from gas collection systems. Volatilization is the primary mechanism for release to air from contaminated surface water. Release to air from contaminated soil can be caused by the volatilization of organics or from wind erosion of particulates (e.g., containing heavy metals). Therefore, information collected from other media investigations can provide useful input data for characterizing releases to air. It may also be efficient to concurrently investigate these media. However, once releases become airborne, the characterization approach presented in this section is applicable.

Releases to air also have the potential for contaminating other media. Releases to air can contaminate soil and surface water via [wet and dry] deposition. It is generally difficult to directly monitor these deposition processes. In these cases, removal rates can be estimated by use of specialized atmospheric dispersion models or by direct measurements of soil and surface water contaminants. Information from the investigation can provide useful input for assessing the significance of atmospheric deposition.

12.3 Characterization of the Contaminant Source and the Environmental Setting

Release investigations can be conducted in an efficient, effective and representative manner if certain information is obtained prior to implementation of the effort. This information consists of both waste/unit characterization and characterization of the environmental setting. Review of information from existing sources can be used to identify data gaps and to initiate data collection activities to fill these data gaps. Waste/unit characterization and characterization of the environmental setting are discussed below:

> Waste and unit specific information. Data on the specific constituents present in the unit that are likely to be released to the air can be used to design sampling efforts and identify candidate constituents to be monitored. This information can be obtained from either a review of the existing information on the waste or from new sampling and analysis. The manner in which the wastes are treated, stored or disposed may have a bearing on the magnitude of air emissions from a unit. In many cases, this information may be obtained from facility records, contact with the manufacturer of any control devices, or, in some cases, from the facility's RCRA permit application.
>
> Environmental setting information. Environmental setting information, particularly climatological data, is essential in characterizing an air release. Climatological parameters such as wind speed and temperature will have a significant impact on the distribution of a release and in determining whether a particular constituent will be released. Climatological and meteorological information for the area in which the facility is located can be obtained either through an onsite monitoring effort or from the National Climatic Data Center (Asheville, NC). The climatologial data should be evaluated considering site topography and other local influences that can affect the data representativeness.

Information pertaining to the waste, unit, and environmental setting can be found in many readily available sources. General information concerning waste/unit characterization is discussed in Section 7. Air specific information is provided in the following discussions.

12.3.1 Waste Characterization

Several waste characteristics contribute to the potential for a waste constituent to be released via the air pathway. These characteristics, in conjunction with the type of unit and its operation, will determine whether a release will be via volatilization of the constituent or as particulate entrainment. Major factors include the types and number of hazardous constituents present, the concentrations of these constituents in the waste(s), and the chemical and physical characteristics of the waste and its constituents. All of these factors should be considered in the context of the specific unit operation involved. It is important to recognize that the constituents of concern in a particulate release may involve constituents that are either sorbed onto the particulate, or constituents which actually comprise the particulate.

12.3.1.1 Presence of Constituents

The composition of the wastes managed in the unit of concern will influence the nature of a release to air. Previous studies may indicate that the constituents are present in the unit or that there is a potential for the presence of these constituents. In determining the nature of a release, it may be necessary to determine the specific waste constituents in the unit if this has not already been done. Guidance on selecting monitoring constituents is presented in Section 3 (and Appendix B); waste characterization guidance is presented in Section 7.

12.3.1.2 Physical/Chemical Properties

The physical and chemical properties of the waste constituents will affect whether they will be released, and if released, what form the release will take (i.e., vapor, particulate, or particulate-associated). These factors are identified in Table 12-3 as a function of emission and waste type. Important factors to consider when assessing the volatilization of a constituent include the following:

- Water solubility. The solubility in water indicates the maximum concentration at which a constituent can dissolve in water at a given temperature. This value can help the investigator estimate the distribution of a constituent between the dissolved aqueous phase in the unit and the undissolved solid or immiscible liquid phase. Considered in combination with the constituent's vapor pressure, solubility can provide a relative assessment of the potential for volatilization of a constituent from an aqueous environment.

- Vapor pressure. This property is a measure of the pressure of vapor in equilibrium with a pure liquid. It is best used in a relative sense;constituents with high vapor pressures are more likely to be released than those with low vapor pressures, depending on other factors such as relative solubility and concentration (e.g., at high concentrations releases can occur even though a constituent's vapor pressure is relatively low).

- Octanol/water partition coefficient. The octanol/water partition coefficient indicates the tendency of an organic constituent to sorb to organic components of soil or waste matrices. Constituents with high octanol/water partition coefficients tend to adsorb readily to organic carbon, rather than volatilizing to the atmosphere. This is particularly important in landfills and land treatment units, where high organic carbon content in soils or cover material can significantly reduce the release potential of volatile constituents.

- Partial pressure. For constituents in a mixture, particularly in a solid matrix, the partial pressure of a constituent will be more significant than pure vapor pressure. A partial pressure measures the pressure which each component of a mixture of liquid or solid substances will exert in order to enter the gaseous phase. The rate of volatilization of an organic chemical when either dissolved in water or present in a solid mixture is charcterized by the partial pressure of that chemical. In general, the greater the partial pressure, the greater the potential for release. Partial pressure values are unique for any given chemical in any given mixture and may be difficult to

TABLE 12-3
PARAMETERS AND MEASURES FOR USE IN EVALUATING POTENTIAL RELEASES OF HAZARDOUS WASTE CONSTITUENTS TO AIR

Emission and Waste Type	Units of Concern[1]	Useful Parameters and Measures
A. Vapor Phase Emissions		
- Dilute Aqueous Solution[2]	Surface Impoundments, Tanks, Containers	Solubility, Vapor Pressure, Partial Pressure[3]
- Conc. Aqueous Solution[2]	Tanks, Containers, Surface Impoundments	Solubility, Vapor Pressure, Partial Pressure, Raoults Law
- Immiscible Liquid	Containers, Tanks	Vapor Pressure, Partial Pressure
- Solid	Landfills, Waste Piles, Land Treatment	Vapor Pressure, Partial Pressure, Octanol/Water Partition Coefficient, Porosity
B. Particulate Emissions		
- Solid	Landfills, Waste Piles, Land Treatment	Particle Size Distribution, Unit Operations, Management Methods

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[1] Incinerators are not specifically listed on this table because of the unique issues concerning air emissions from these units. Although Incinerators can burn many forms of waste, the potential for release from these units is primarily a function of incinerator operating conditions and emission controls, rather than waste characterisitics.

[2] Although the octanol/water partition coefficient of a constituent is usually not an important characteristic in these waste streams, there are conditions where it can be critical. Specifically, in waste containing high concentrations of organic particulates, constituents with high octanol/water partition coefficients will adsorb to the particulates. They will become part of the sludge or sediment matrix, rather than volatilizing from the unit.

[3] Applicable to mixtures of volatile components.

obtain. However, when waste characterization data is available, partial pressure can be estimated using methods commonly found in engineering and environmental science handbooks.

- Henry's Law constant. Henry's law constant is the ratio of the vapor pressure of a constituent to its aqueous solubility (at equilibrium). This constant can be used to assess the relative ease with which the compound may vaporize from the aqueous phase. It is applicable only for low concentration (i.e., less than 10 percent) wastes in aqueous solution and will be most useful when the unit being assessed is a surface impoundment or tank containing dilute wastewaters. The potential for significant vaporization increases is the value for Henry's Law Constant increases; when it is greater than 10E-3, rapid volatilization will generally occur.

- Raoult's Law. Raoult's Law accurately predicts the behavior of most concentrated mixtures of water and organic solvents (i.e., solutions over 10% solute). According to Raoult's Law, the rate of volatlization of each chemical in a mixture is proportional to the product of its concentration in the mixture and its vapor pressure. Therefore, Raoult's Law can be used to characterize volatilization potential. This will be expecially useful when the unit of concern entails container storage, tank storage, or treatment of concentrated waste streams.

A summary of some of these factors for several constituents is given in Tables 12-4 and 12-5. The following document contains a compilation of chemical-physical properties for several hundred constituents. Additional references for these data are provided in Section 7.

U.S. EPA. 1987. Hazardous Waste Treatment Storage and Disposal Facilities (TSDF) - Air Emission Models. Office Air Quality Planning and Standards. Research Triangle Park, N.C. 27711

For airborne particluates, the particle size distribution plays an important role in both dispersion and actual inhalation exposure. Large particles tend to settle out of the air more rapidly than small particles. Very small particles (i.e., those that are less

TABLE 12-4
PHYSICAL PARAMETERS OF VOLATILE HAZARDOUS CONSTITUENTS

Hazardous constituent	Molecular weight	Vapor pressure at 25°C (mmHg)	Solubility at 25°C (mg/l)	Henry's Law constant (atm^{-3}/mol)
Acetaldehyde	44	915	1.00E + 06	9.50E-05
Acrolein	56	244	4.00E + 05	4.07E-05
Acrylonitrile	53	114	7.90E + 04	8.80E-05
Allylchloride	76.5	340		340E-01
Benzene	78	95	1.78E + 03	5.50E-03
Benzyl chloride	126.6	1.21	1.00	
Carbon tetrachloride	154	109	8.00E + 02	2.00E-02
Chlorobenzene	112	12	5.00E + 02	2.00E-03
Chloroform	119	192	8.00E + 03	3.00E-03
Chloroprene	88.5	215		
Cresols	108	0.4	2.00E + 04	4.60E-07
Cumene (isopropylbenzene)	120	4.6	50.0	2.00E-04
1,4-dichlorobenzene	147	1.4	49.00	
1,2-dichloroethane	99	62	8.69E + 03	1.00E-04
Dichloromethane	85	360	2.00E + 04	2.00E-03
Dioxin	178	7.6E-7	3.17E-04	1.20E-03
Epichlorohydrin	92.5	13	6.00E + 04	3.08E-05
Ethylbenzene	106	10	152	7.00E-03
Ethylene oxide	44	1,095	1.35E + 05	
Formaldehyde	30	3,500	3.00E + 05	
Hexachlorobutadiene	261	0.15		
Hydrogen cyanide	27	726		
Hydrogen flouride	20	900		
Hydrogen sulfide	34	15,200		
Hexachlorocyclopentadiene	273	0.03		
Maleic anhydride	98	0.3	1.63E + 05	
Methyl acetate	74	170	3.19E + 05	1.00E-04
N-Dimethylnitrosamine	81	3.4		
Naphthlene	123	0.23		
Nitrobenzene		0.3	1.90E + 03	1.30E-05
Nitrosomorpholine		5.3		
Phenol	94	0.34	9.30E + 04	1.02E-05
Phosgene	98	1,300		
Phthalic anhydride	148	0.03	6.17E + 03	9.00E-07
Propylene oxide		400		
1,1,2,2-tetrachloroethane	168	9	2.90E + 03	2.00E-04
Tetrachloroethylene	166	15	200	
Toluene	92	30	534	5.00E-03
1,1,1-trichloroethane	133	123	720	2.15E-02
Trichloroethylene	131	90	1.10E + 03	8.92E-03
Vinylchloride	62.5	2,600	6.00E + 03	1.90E-01
Vinylidenechloride	97	500		
Xylenes	106	8.5	1.00	4.04E-04

TABLE 12-5
PHYSICAL PARAMETERS OF PCB MIXTURES*

Arochlor (PCB)	Vapor pressure at 25°C (atm)	Solubility at 25°C (mg/l)	Henry's Law constant (atm-m^3/mol)
1242	2.19E-07	2400	238E-08
1248	1.02E-07	520	1.02E-08
1254	1.85E-08	120	1.40E-08
1260	5.17E-09	30	6.46E-08

* All values estimated based on calculations.

than 2.5 to 10 microns in diameter) are considered to be respirable and thus present a greater health hazard than the larger particles. Therefore, the source of the release should be examined to obtain information on particle size. Process information may be sufficient to grossly characterize the potential for particulate formation. For example, the presence of ash materials and similar wastes would be a case in which particulate emissions would be of concern.

12.3.2 Unit Characterization

Different types of units may have differing release potentials. The particular type of unit, its configuration, and its operating conditions will have a great effect on the nature, extent, and rate of the release. These practices or parameters should be determined and reasonable worst-case operating practices or conditions should also be identified prior to initial sampling.

12.3.2.1 Type of Unit

The type of unit will affect its release potential and the types of releases expected. For the purpose of this guidance, units have been divided into three general types with regard to investigating releases to air. These are:

- Area sources having solid surfaces, including land treatment facilities, surfaces of landfills, and waste piles;
- Point sources, including vents, (e.g., breathing vents from tanks) and ventilation outlets from enclosed units (e.g., container handling facilities or stacks); and
- Area sources having liquid surfaces, including surface impoundments and open-top tanks.

The following discussion provides examples for each of these unit types and illustrates the kind of data that should be collected prior to establishing a sampling plan. Table 12-6 indicates types of releases most likely to be observed from each of these example unit types. It should also be recognized that releases to air can be continuous or intermittent in nature.

TABLE 12-6
SUMMARY OF TYPICAL UNIT SOURCE TYPE AND AIR RELEASE TYPE

Typical Unit Type	Source Type			Potential Phase of Release	
	Area Sources with Liquid Surface	Area Sources with Solid Surface	Point Sources	Vapor	Particulate
Waste Piles		X		X	X
Land Treatment Units		X		X	X
Landfills		X	X	X	X
Drum Handling Facilities			X	X	X
Tanks	X		X	X	
Surface Impoundments	X			X	
Incinerators*			X	X	X

* Includes units (e.g., garbage incinerators) not covered by 40 CFR Part 264, Subpart O which pertains to hazardous waste incinerators.

Waste piles--Waste piles are primarily sources of particulate releases due to entrainment into the air of solid particles from the pile. Waste piles are generally comprised of dry materials which may be released into the air by wind or operational activities. The major air contaminants of concern from waste piles will be those compounds that are part of or have been adsorbed onto the particulates. Additionally, volatilization of some constituents may occur. Important unit factors include the waste pile dimensions (e.g., length, width, height, diameter and shape), and the waste management practices (e.g., the frequency and manner in which the wastes are applied to the pile and whether any dust suppression procedures are employed). The pile dimensions determine the surface area available for wind erosion. Disturbances to the pile can break down the surface crust and thus increase the potential for particulate emissions. Dust suppression activities, however, can help to reduce particulate emissions.

Land treatment units--Liquid or sludge wastes may be applied to tracts of soil in various ways such as surface spreading of sludges, liquid spraying on the surface, and subsurface liquid injection. These methods may also involve cultivation or tilling of the soil. Vapor phase and particulate contaminant releases are influenced by the various application techniques. Particulate or volatile emission releases are most likely to occur during initial application or during tilling, because tilling keeps the soil unconsolidated and loose, and increases the air to waste surface area.

Important unit factors in assessing an air release from a land treatment unit include:

- Waste application method - Liquid spraying applications tend to minimize particulate releases while increasing potential volatile releases. Subsurface applications generally reduce the potential for particulate and volatile releases.

- Moisture content of the waste - Wastes with high moisture content will be less likely to be released as particulates; however, a potential vapor phase release will become more likely.

- Soil characteristics - Certain constituents, such as hydrophobic organics, will be more likely to bound to highly organic soils than non-organic soils. Therefore, releases of these types of constituents are most likely to be associated with particulate emissions.

Landfills--Landfills can result in particulate and vapor phase releases. This process generally involves placement of waste in subsurface disposal cells and subsequent covering of the waste with uncontaminated soil. Landfill characteristics that can affect contaminant release include:

- Porosity and moisture content of the soil or clay covering can influence the rate at which vapor phase releases move through the soil towards the surface. Finer soils with lower porosities will generally slow movement of vapors through the unit. The frequency of applying soil cover to the open working face of a landfill will also affect the time of waste exposure to the air.

- Co-disposal of hazardous and municipal wastes will often increase the potential for vapor phase releases, because biodegradation of municipal wastes results in the formation of methane gas as well as other volatile organics. Methane gas may act as a driving force for release of other volatile hazardous components that may be in the unit (See Section 11 - Subsurface gas.)

- Landfill gas vents, if present, can act as sources of vapor phase emissions of contaminated landfill gases.

- Leachate collection systems can be sites of increased vapor phase emissions due to the concentrated nature of the leachate collected. Open trenches are more likely to be emission sources than underground collection sumps due to the increased exposure to the atmosphere.

- Waste mixing or consolidation areas where bulk wastes are mixed with soil or other materials (e.g., fly ash) prior to landfilling can be contributors to both particulate and vapor phase air releases. Practices such as spreading materials on the ground to release moisture prior to landfilling will also increase exposure to the atmosphere.

Drum handling facilities--Emissions from drum or container handling areas can result from several types of basic operations. Frequently, emissions from these operations are vented to the air through ducts or ventilation systems. Air sampling to assess emissions from these operations may include sampling of the control device outlets, the workplace atmosphere at each operation, or the ambient air downwind of the unit. Factors which effect emissions include:

- Filling operations can be a major source of either vapor or particulate emissions due to agitation of the materials during the filling process. Spillage which occurs during loading may also contribute to emissions. Organic waste components with high volatility will readily vaporize into the air. Similarly, particulate matter can be atmospherically entrained by agitation and wind action. The emission potential of filling operations will be affected by exposure to ambient air. Generally, fugitive emissions from an enclosed building will be less than emissions created during loading in an open structure.

- Cleaning operations can have a high potential for emissions. These emissions may be enhanced by the use of solvents or steam cleaning equipment. The waste collection systems at these operations usually provide for surface runoff to open or below ground sumps, which can also contribute to air emissions.

- Volatilization of waste components can also occur at storage units. Since it is common practice to segregate incompatible wastes during storage, the potential for air releases may differ within a storage unit depending on the nature of the wastes stored in any particular area. The most common source of air emission releases from drum storage areas is spills from drums ruptured during shipping and handling.

- For offsite facilities, storage areas frequently are located where drums are sampled during the waste testing/acceptance process. This process involves drum opening for sampling and could also include spillage of waste materials on the ground or floor.

Important release information includes emission rates, and data to estimate release rise (e.g., vent height and diameter as well as vent exit temperature and velocity). Information pertaining to building dimensions/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

Tanks--Tanks can emit volatile waste components under various circumstances. A major determinant of any air emission will be the type of tank being studied. Closed or fixed roof storage tanks will most likely exhibit less potential for air emissions than open topped tanks. Some tanks are equipped with vapor recovery systems that are designed to reduce emissions. Important process variables for understanding air emissions from tanks can be classified as descriptive and operational variables:

- Descriptive variables include - type, age, location, and configuration of the tank.

- Operational variables include - aeration, agitation, filling techniques, surface area, throughput, operating pressure and temperature, sludge removal technique and frequency, cleaning technique and frequency, waste retention and vent pipe dimensions and flow rate.

Important release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity). Information pertaining to building dimensions/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

Surface impoundments--Surface impoundments are similar in many ways to tanks in the manner in which air emissions may be created. Surface impoundments are generally larger, at least in terms of exposed surface area, and are generally open to the atmosphere. The process variables important for the evaluation of releases to air from surface impoundments can also be classified as descriptive and operational.

- Descriptive parameters include - dimensions, including length, width, and depth, berm design, construction and liner materials used, and the location of the unit on the site.

- Operational parameters include - freeboard filling techniques (in particular, splash versus submerged inlet), depth of liquid and sludge layers, presence of multiple liquid layers, operating temperature, sludge removal techniques and frequency, cleaning technique and frequency, presence of aerators or mixers, biological activity factors for biotreatment, and the presence of baffles, oil layers, or other control measures on the liquid surface. (These factors are relevant to some tanks as well.)

Some surface impoundments are equipped with leak collection systems that collect leaking liquids, usually into a sump. Air emissions can also occur from these sumps. Sump operational characteristics and dimensions should be documented and, if leaks occur, the volume of material entering the sump should be documented. (These factors are relevant to some tanks as well.)

Incinerators - Stack emissions from incinerators (i.e., incinerator units not addressed by RCRA in Part 264, Subpart 0, e.g., municipal refuse incinerators) can contain both particulates and volatile constituents. The high temperatures of the incineration process can also cause volatilization of low vapor pressure organics and metals. Additional volatile releases can occur from malfunctioning valves during incinerator charging. The potential for air emissions from these units is primarily a function of incinerator operating conditions and emission controls. Important unit release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity), as well as building dimensions/orientation of the unit and nearby structures. This information is needed to assess the aerodynamic behavior of the stack/vent release and for input to atmospheric dispersion models.

12.3.2.2 Size of Unit

The size of the unit(s) of concern will have an important impact on the potential magnitude of a release to air. The release of hazardous constituents to the air from an area source is often directly proportional to the surface area of the unit, whether this surface area is a liquid (e.g., in a tank) or a solid surface (e.g., a land treatment unit). The scope of the air investigation may be a function of the size of the unit. Generally, more sampling locations will be required as the unit increases in size, due primarily to increased surface area. Also, as the total amount of waste material present in a particular unit increases, it will represent a larger potential reservoir or source of constituents which may be released.

Scaling factors, such as surface area to volume ratios should also be evaluated. One large waste pile, for instance, can exhibit a lower ratio of surface area to total volume than the sum of two smaller piles in which the total volume equals that of the larger pile. Other units such as tanks may exhibit a similar economy of surface area, based on the compact geometry of the unit.

Because releases to air generally occur at the waste/atmosphere interface, surface area is generally a more important factor than total waste volume. Consequently, operations that increase the atmosphere/waste interface, such as agitation or aeration, splash filling, dumping or filling operations, and spreading operations will tend to increase the emission rate. Total emissions, however, will be a function of the total mass of the waste constituent(s) and the duration of the release.

For point sources, the process or waste throughput rate will be the most important unit information needed to evaluate the potential for air emissions (i.e., stack/vent releases).

12.3.2.3 Control Devices

The presence of air pollution control devices on units can have a major influence on the nature and extent of releases. Control devices can include wet or dry scrubbers, electrostatic precipitators, baghouses, filter systems, wetting practices for solid materials, oil layers on surface impoundments, charcoal or resin absorption systems, vapor flares, and vapor recovery systems. Many of these controls systems can be installed on many of the unit types discussed in this section. Due to the variety of types of devices and the range of operational differences, an in depth discussion of individual control devices is not presented here. Additional information on control technologies for hazardous air pollutants is available in the following references:

U.S. EPA. 1986. Handbook - Control Technologies for Hazardous Air Pollutants. EPA/62516-86/014. NTIS PB 86-167020 and PB 86-167038. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. 1986. Evaluation of Control Technologies for Hazardous Air Pollutants: Volume 1 - Technical Report. EPA/600/7-86/009a. NTIS PB 86-167020. Volume 2 - Appendices. EPA/600/7-86/009b. NTISPB 86-167038. Office of Research and Development, Research Triangle Park, N.C. 27711.

If a control device is present on the unit of concern, descriptive and operational characteristics of the unit/control device combination should be reviewed and documented. In many cases, performance testing of these devices has been conducted after their installation on the unit(s). Information from this testing may help to quantify releases to air from the unit(s); however, this testing may not have been performed under a "reasonable worst-case" situation. The conditions under which the testing was performed should be documented.

12.3.2.4 Operational Schedules

Another characteristic which can affect the magnitude of a release to air from a unit is the unit's operational schedule. If the unit is operational on a part time or batch basis, the emission or release rate should be measured during both operational and non-operational periods. In contrast to batch operations, emission or release rates from continuous waste management operations may be measured at any time.

12.3.2.5 Temperature of Operation

Phase changes of liquids and solids to gases is directly related to temperature. Therefore, vapor phase releases to air are directly proportional to process temperature. Thus, it is important to document operational temperature (i.e., waste temperature) and fluctuations to enhance the understanding of releases to air from units. Particular attention should be paid to this parameter in the review of existing data or information regarding the operation of the unit.

The release rate of volatile components also generally increases with temperature. Frequently, the same effect is observed for particulates, because entrainment is enhanced as materials are dried. Thus, the evaporation of any water from solids, which generally increases as temperature increases, will likely increase the emissions of many particulates in the waste streams. Evaporation of water may also serve to concentrate wastes, leading to conditions more conducive to vapor phase releases to air. It should also be noted that the destruction efficiency of incinerators is also a function of temperature (i.e., higher temperatures are generally associated with greater destruction efficiency).

12.3.3 Characterization of the Environmental Setting

Environmental factors can influence not only the rate of a release to air but also the potential for exposure. Significant environmental factors include climate, soil conditions, terrain and location of receptors. These factors are discussed below:

12.3.3.1 Climate

Wind, atmospheric stability and temperature conditions affect emission rates from area sources as well as atmospheric dispersion conditions for both area and point sources. Historical summaries of climatic factors can provide a basis to assess the long-term potential for air emissions and to characterize long-term ambient concentration patterns for the area. Short-term measurements of these conditions during air monitoring will provide the meteorological data needed to interpret the concurrent air quality data. Meteorological monitoring procedures are discussed in Section 12.6. Available climatic information, on an annual and monthly or seasonal basis, should be collected for the following parameters:

- Wind direction and roses (which affects atmospheric transport, and can be used to determine the direction and dispersion of release migration);
- Mean wind speeds (which affects the potential for dilution of releases to air);
- Atmospheric stability distributions (which affects dispersion conditions);
- Temperature means and extremes (which affects the potential for volatilization, release rise and wind erosion);
- Precipitation means (which affects the potential for wind erosion of particulates);
- Atmospheric pressure means (which affects the potential for air emissions from landfills); and
- Humidity means (which can affect the air collection efficiencies of some adsorbents - see Section 12.6).

The primary source of climate information for the United States is the National Climatic Data Center (Asheville, NC). The National Climatic Data Center can provide climate summaries for the National Weather Service station nearest to the site of interest. Standard references for climatic information include the following:

National Climatic Data Center. Local Climatological Data - Annual Summaries with Comparative Data, published annually. Asheville, NC 28801.

National Climatic Data Center. Climates of the States. 1973. Asheville, NC 28801.

National Climatic Data Center. Weather Atlas of the United States. 1968. Asheville, NC 28801.

The climatological data should be evaluated considering the effects of topography and other local influences that can affect data representativeness.

A meteorological monitoring survey should be conducted prior to ambient air monitoring to establish the local wind flow patterns and for determining the number and locations of sampling stations. The survey results will be used to characterize local prevailing winds and diurnal wind flow patterns (e.g., daytime upslope winds, nighttime downslope winds, sea breeze conditions) at the site. The survey should be conducted for a one-month period and possibly longer to adequately characterize anticipated wind patterns during the air monitoring program. Inland, flat terrain conditions may not necessitate an onsite meteorological monitoring survey if representative data are available from previous onsite studies or from National Weather Service stations.

The meteorological monitoring data collected during the initial air monitoring phase can serve as a basis for the placement of air sampling stations during any subsequent monitoring phases.

12.3.3.2 Soil Conditions

Soil conditions (e.g., soil porosity) can affect air emissions from landfills and the particulate wind erosion potential of contaminated surface soils. Soil conditions pertinent to characterizing the potential for air emissions include the following:

- Soil porosity (which affects the rate of potential gaseous emissions);
- Particle size distribution (which affects the potential for particulate emissions from contaminated soils); and
- Contaminant concentrations in soil (i.e., potential to act as air emission sources).

Soil information characterization information is presented in Section 9.

12.3.3.3 Terrain

Terrain features can significantly influence the atmospheric transport of air emissions. Terrain heights relative to release heights will affect groundlevel concentration. Terrain obstacles such as hills and mountains can divert regional winds. Likewise, valleys can channel wind flows and also limit horizontal dispersion. In addition, complex terrain can result in the development of local diurnal wind circulations and affect wind speed, atmospheric turbulence and stability conditions. Topographic maps of the facility and adjacent areas are needed to assess local and regional terrain. Guidance on the appropriate format and sources of topographic and other maps is presented in Section 7 and Appendix A.

12.3.3.4 Receptors

Information concerning the locations of nearby buildings and the population distribution in the vicinity of the site are needed to identify potential air-pathway receptors. This receptor information provides a basis for specifying strategies for air sampling locations. Environmental and human receptor information is needed to assess potential air-pathway exposures and to determine air monitor placement. Such information may include:

- A site boundary map;

- Location of nearest buildings and residences for each of the sixteen 22.5 degree sectors which correspond to major compass points (e.g., north, north-northwest);

- Location of buildings and residences that correspond to the area of maximum offsite groundlevel concentrations based on preliminary modeling estimates (these locations may not necessarily be near the site boundary for elevated releases); and

- Identification of nearby sensitive receptors (e.g., nursing homes, hospitals, schools, crticial habitat of endangered or threatened species).

The above information should be considered in the planning of an air monitoring program. Additional guidance on receptor information is provided in Section 2.

12.3.4 Review of Existing Information

The review of existing air monitoring data entails both summarizing the reported air contaminant concentrations as well as evaluating the quality of these data. Air data can be of many varieties and of varying utility to the RFI process. One of the most basic parameters to review in any type of air data should be the validity of the sampling locations used during the collection of the data. The results of previous investigations should be assessed with respect to the upwind-downwind pattern around the unit to determine the likelihood that the sampling devices would have measured releases from the unit of concern. For relatively simple sites (e.g., flat terrain, constant wind speed and direction), this determination should be fairly straight-forward; however, for complex sites (e.g., complex terrain, variable winds, multiple sources, etc.), assessing the appropriateness of past sampling locations should consider such factors as potential interferences that may not have been addressed by the sampling scheme.

The most useful monitoring data are compound-specific results which can be associated with the unit being investigated, or, for point sources (such as vent stacks or ventilation system outlets), direct measurements of the exhaust prior to its release into the atmosphere. Because the hazardous properties and health and environmental criteria are compound-specific, general compound category or class data (e.g., hydrocarbon results) are less meaningful. Any existing air data should also be described and documented as to the sampling and analysis methods utilized, the associated detection limits, precision and accuracy, and the results of QA/QC analyses conducted. Results reported as non-detected (i.e., not providing numerical detection limits) are likely to be of no value.

In addition, available upwind and downwind ambient air data should be evaluated to determine if the contamination is due to releases from the unit. If background data are available for the unit of concern, the data will be of much greater use in the planning of additional air monitoring tasks. Upwind data (to characterize ambient air background levels) are important for evaluating if downwind contamination can be attributed to the unit of concern. If background data are not available, the existing downwind air concentration data will be of less value in characterizing a release; however, the lack of background data does not negate the utility of the available monitoring data.

Data may also be available from air monitoring studies that did not focus directly on releases from a unit of concern. Many facilities conduct onsite health and safety programs, including routine monitoring of air quality for purposes of evaluating worker exposure. This type of data may include personnel hygiene monitoring results from personal sampling systems worn by employees as they perform their jobs, general area monitoring of zones at which hazardous operations are conducted, or actual unit-emission monitoring. The detection limits of these methods (generally in parts per million) are frequently higher than are needed for RFI purposes. However, this type of industrial hygiene monitoring is frequently compound-specific, and can be useful in qualitatively evaluating the air emissions from particular sources.

Indoor air monitoring, generally only applicable to units that are enclosed in a building (e.g., drum handling areas or tanks), often includes flow monitoring of the ventilation system. Monitoring of hoods and ductwork systems may have been conducted to determine exchange time and air circulation rates. These flow determinations could prove to be useful in the evaluation of air emissions measurements during the RFI.

Another important aspect of the existing data review is to document any changes in composition of the waste managed in the unit of concern since the air data were collected. Also, changes in operating conditions or system configuration for waste generation and/or unit functions could have major effects on the nature or extent of releases to air. If such operational or waste changes have occurred, they should be summarized and reviewed to determine their role in the evaluation of existing data. This summary and review will not negate the need to take new samples to characterize releases from the unit. However, such information can be useful in the planning of the new air monitoring activities.

12.3.5 Determination of "Reasonable Worst-Case" Exposure Period

A "reasonable worst-case" exposure period over a 90 day period should be identified to aid in planning the air monitoring program. Determination of reasonable worst-case exposure conditions is dependent on seasonal variations in emission rates and dispersion conditions.

The selection of the "reasonable worst-case" 90-day exposure period for the conduct of air monitoring should account for the following factors:

- For vapor phase releases, wind speed and temperature are the key factors affecting releases from the unit. In general, the higher the temperature and wind speed, the greater the rate of volatilization of constituents of concern from the waste. This process is tempered, however, by the fact that at higher windspeeds, dispersion of the release is generally greater, resulting in lower downwind concentrations at potential exposure points.

- For particulate releases, wind speed is the key meteorological factor. The amount of local precipitation contributing to the degree of moisture of the waste may also be important. In general, the higher the windspeed, and the drier the waste, the greater will be the potential for particulate release. As with vapor phase releases, higher wind speeds may also lead to greater dispersion of the release, resulting in lower downwind concentrations.

- For point source releases, increased wind speeds and unstable atmospheric conditions (e.g., during cloudless days) enhance dispersion but also tend to reduce plume height and can lead to relatively high groundlevel concentrations.

- Constituent concentrations at any downwind sector will also be directly affected by the wind direction and frequency.

Air emission release rate models and atmospheric dispersion models can be used to identify reasonable worst-case exposure conditions (i.e., to quantitatively account for the above factors). For this application it is recommended that the modeling effort be limited to a screening/sensitivity excercise with the objective of obtaining "relative" results for a variety of source and meteorological scenarios. By comparing results in a relative fashion, only those input meteorological parameters of greatest significance (e.g., temperature, wind speed and stability) need to be considered. Case Study number 15 in Volume IV (Case Study Examples), illustrates this approach.

In general, the summer season will be the "reasonable worst-case" exposure period at most sites because of relatively high temperatures and low windspeeds. Spring and fall are also candidate monitoring seasons that should be evaluated on a site-specific basis. Winter is generally not a prime season for air monitoring due to of the lower temperatures and higher wind speeds.

12.4 Design of a Monitoring Program to Characterize Releases

Based on gathering of the information previously described, including determination of reasonable worst-case scenarios as discussed in the previous section, monitoring procedures can be developed. This section discusses the recommended monitoring approaches.

Primary elements in designing a monitoring system include:

- Establishing monitoring objectives;
- Determining monitoring constituents of concern;
- Monitoring schedule;
- Monitoring approach; and
- Monitoring locations.

Each of these elements should be addressed to meet the objectives of the initial monitoring phase, and any subsequent phases that may be necessary. These elements are described in detail below.

12.4.1 Objectives of the Monitoring Program

The overall goal of the air monitoring program is to determine concentrations at actual offsite receptor locations as input to the health and environmental assessment process. As discussed previously, the monitoring program may be conducted in a phased approach, using the results of initial monitoring to determine the need for and scope of subsequent monitoring.

Principal objectives of both the initial and subsequent monitoring phases are:

- Identification of constituents;
- Characterization of long-term ambient constituent concentrations (based on a "reasonable worst case" exposure period) at:
  - the unit boundary to maximize the potential for release detection
  - the facility property boundary
  - actual offsite receptor locations
  - areas upwind of the release source in order to characterize background concentrations; and
- Collection of meteorological data during the monitoring period to aid in evaluating the air monitoring data

Atmospheric dispersion modeling may be needed to estimate concentrations at offsite receptor locations if monitoring at offsite locations is not practical, as discussed previously.

Subsequent monitoring may be necessary if initial monitoring and modeling data were not sufficient to characterize long-term ambient constituent concentrations at actual offsite receptors. Subsequent monitoring may also be required to determine the effectiveness of interim control measures, if applied.

12.4.2 Monitoring Constituents and Sampling Considerations

Sampling and analysis may be conducted for all appropriate Appendix VIII constituents that have an air pathway potential (See Section 3 and Appendix B). An alternative approach is to use unit and waste-specific information to identify constituents that are not expected to be present and thus, reduce the list of target monitoring constituents. For example, the industry specific monitoring constituent lists presented in Appendix B, List 3 can be used to identify appropriate air monitoring constituents for many applications (especially for units that serve only one or a limited number of industrial categories).

Results from the screening sampling phase (as defined later in Section 12.4.4.1), may also be used as a basis for selection of monitoring constituents. These short-term air sampling results may confirm/identify appropriate monitoring constituents for the unit of concern.

12.4.3 Meteorological Monitoring

Monitoring of onsite meteorological conditions should be performed in concert with other monitoring activities to aid in the interpretation of air-quality monitoring data. Results of such monitoring can serve as input for dispersion models, and can be used to assure that the monitoring effort is conducted during the appropriate meteorological conditions (e.g., "reasonable worst case" period for initial monitoring).

12.4.3.1 Meteorological Monitoring Parameters

The following meteorological parameters should be routinely monitored while collecting ambient air samples:

- Horizontal wind speed and direction;
- Ambient temperature;
- Atmospheric stability (e.g., based on the standard deviation of horizontal wind direction or alternative standard methodologies);
- Precipitation measurements if representative National Weather Service data are not available; and

- Atmospheric pressure (e.g., for landfill sites or contaminated soils) if representative National Weather Service data are not available.

It is recommended that horizontal wind speed and direction, and air temperature be determined onsite with continuous recording equipment. Estimates from offsite monitors are not likely to be representative for all of the conditions at the site. Input parameters for dispersion models, if appropriate, should be reviewed prior to conducting the meteorological data collection phase to insure that all necessary parameters are included.

Field equipment used to collect meteorological data can range in sophistication from small, portable, battery-operated units with wind speed and direction sensors, to large, permanently mounted, multiple sensor units at varying heights. Individual sensors available can collect data on horizontal wind speed and direction, three-dimensional wind speed, air temperature, humidity, dew point, and mixing height. From such data, variables for dispersion models such as wind variability and atmospheric stability can be determined. Additional guidance on meteorological measurements can be obtained from:

U.S. EPA. February 1983. Quality Assurance handbook for Air Pollution Measurement Systems: Volume IV. Meteorological Measurements. EPA-600/4-82-060. NTIS PB 254-658/8. Office of Research and Development. Research Traingle Park, N.C 27711.

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EPA-450/2-78-027R. NTIS PB 86-245248.Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

Appropriate performance specifications for monitoring equipment are given in the following document:

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80/012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

12.4.3.2 Meteorological Monitor Siting

Careful placement of meteorological monitoring equipment (e.g., sensors) is important in gathering relevant data. The objective of monitoring tower placement is to position sensors to obtain measurements representative of the conditions that determine atmospheric dispersion in the area of interest. The convention for placement of meteorological monitoring equipment is:

- At or above a height of 10 meters above ground; and
- At a horizontal distance of 10 times the obstruction height from any upwind obstructions.

In addition, the recommendations given in Table 12-7 should be followed to avoid effects of terrain on meteorological monitors.

Depending on the complexity of the terrain in the area of interest and the parameters being measured, more than one tower location may be necessary. Complex terrain can greatly influence the transport and diffusion of a contaminant release to air so that one tower may not be able to account for these influences. The monitoring station height may also vary depending on source characteristics and logistics. Heights should be selected to minimize near-ground effects that are not representative of conditions in the atmospheric layer into which a constituent of concern is being released.

A tower designed specifically to mount meteorological instruments should be used. Instruments should be mounted on booms projecting horizontally out from the tower at a minimum distance of twice the tower diameter. Sound engineering practice should be used to assure tower integrity during all meteorologic conditions.

Further guidance on siting meteorological instruments and stations is available in the following publications:

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

TABLE 12-7
RECOMMENDED SITING CRITERIA TO AVOID TERRAIN EFFECTS

Distance from Tower (meters)	Maximum Acceptable Construction or Vegetation Height (meters)
0 - 15	0.3
15 - 30	0.5 - 1.0
30 - 100	3
100 - 300	10

U.S. EPA. February 1983. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV. Meteorological Measurements. EPA-600/4-82-060. NTIS PB 254-658/8. Office of Research and Development. Research Triangle Park, N.C. 27711.

12.4.4 Monitoring Schedule

Establishment of a monitoring schedule is an important consideration in developing a monitoring plan. When appropriate, air monitoring should coincide with monitoring of other media (e.g., subsurface gas, soils, and surface water) that have the potential for air emissions. As with all other aspects of the monitoring program, the objectives of monitoring should be considered in establishing a schedule. As indicated previously, monitoring generally consists of screening sampling, initial monitoring, and subsequent monitoring. The monitoring schedule during each of these phases is discussed below.

12.4.4.1 Screening Sampling

A limited screening sampling effort may be necessary to focus the design of subsequent monitoring phases. This screening phase can also be used to verify the existence of a release to air and prioritize the major release sources at the facility. Screening sampling should be used to characterize air emissions (e.g., by using total hydrocarbon measurements as an indicator), and to confirm/identify the presence of candidate constituents. Screening samples should generally consist of source emissions measurements or ambient air samples collected at or in close proximity to the source. This approach will provide the best opportunity for detection of air emission constituents. (A discussion of available screening methods is discussed in Section 12.6.) An alternative screening approach involves collection of a limited number of air samples to facilitate the analysis of a wide range of constituents (e.g., collection via Tenax adsorption tubes or whole air sampling with analysis by GC/MS - see Section 12.6).

The screening study should generally involve collection of a limited number of grab or time-integrated samples (several minutes to 24-hours) for a limited time period (e.g., one to five days). Sampling should be conducted during emission/dispersion conditions that are expected to result in relatively high concentrations (as discussed in Section 12.3.5). Screening results should be interpreted considering the representativeness of the waste and unit operations during the sampling, and the detection capabilities of the screening methodology used.

12.4.4.2 Initial Monitoring

The primary objective of initial monitoring is to characterize long-term exposures that may be associated with air emissions from the unit under reasonable worst-case conditions. A schedule should be proposed that will provide an adequate degree of confidence that those compounds that may be released will be detected. A recommended sampling schedule for meeting this objective is given below:

- Meteorological monitoring - 90 days continuous monitoring.
- Air Monitoring (Alternative 1) -90 days:
    - Analysis of 24-hour time integrated samples for target constituents every day during the 90-day period (total of 90 samples)
- Air Monitoring (Alternative 2) -90 days:
    - Analysis of 24-hour integrated samples for target constituents every sixth day (total of 15 samples per station resulting in a total of 15 days of monitoring coverage); and
    - Analysis of a five-day composite sample at each station (consisting of five 24-hour integrated samples), or intermittent sampling (e.g., a continuing cycle of one minute of sampling and five minutes of off-time), during a five-day period (total of 15 additional samples per station, which results in 75 days of monitoring coverage).
- Emission rate monitoring - 1 to 3 days (for selected cases such as point sources, or area sources (such as closed landfills) with variable spatial distribution of waste, for which ambient monitoring detection limits are expected to be less than constituent concentrations).

The 90-day monitoring program (i.e., Alternatives 1 and 2) will facilitate collecting samples over a wide range of emission and dispersion conditions. The 90-day period should be selected, as previously discussed, to coincide with the expected season of highest ambient concentrations. Meteorological monitoring should be continuous and concurrent with this 90-day period to adequately characterize dispersion conditions at the site and to provide meteorological data to support interpretation of the air-quality monitoring data.

Alternative 2 air monitoring approach consists of analyzing 24-hour time-integrated samples every sixth day, plus analyzing the equivalent of a five day time-integrated sample for the remaining portions of each 6-day monitoring cycle throughout the 90-day period. Analysis of the 24-hour time-integrated samples provides the basis to detect high concentration short-term events. These high concentration events may result in the mathematical calculation of an average long-term concentration during the 90-day period that might otherwise not be possible to quantify (i.e., would be less than the analytical detection limit). The five-day time-integrated samples provide an efficient basis to achieve continuous air monitoring during the "reasonable worst case" 90-day monitoring period.

The collection of a time-integrated sample based on continuous monitoring for several days can result in technical difficulties (e.g., poor collection efficiencies for volatile constituents or large sample volumes). The application of five-day composite samples at each station, or intermittent sampling during the five days, results in continuous monitoring coverage during the 90-day period and facilitates the characterization of long-term exposure levels.

Although there are some limitations associated with composite/intermittent sampling (e.g., the potential for sample degradation), the 24-hour samples collected every sixth day will provide a second data set for characterizing ambient concentrations. Although the results of the two data sets should not be directly combined (because of the different sampling periods) they provide a comprehensive technical basis by which to evaluate long-term exposure conditions.

Emission rate monitoring may be necessary to characterize a release if ambient levels are expected to be less than analytical detection limits. This approach involves stack or vent emission monitoring for point sources. Point source monitoring is not dependent on meteorological conditions. However, emission rate monitoring for both point and area sources should be conducted during typical or "reasonable worst case" conditions. Emission rate monitoring for area sources should not be conducted during or immediately following precipitation or if hourly average wind speeds are greater than 15 miles per hour. It should also be noted that soil or cover material (if present) should be allowed to dry prior to continuing monitoring operations, as volatilization decreases under saturated soil conditions. In these cases, the monitoring should be interrupted and resumed as soon as possible after the unfavorable conditions pass. Similarly, operational interruptions such as unit shutdown should also be factored into the source sampling schedule.

Point source emission sampling generally requires only a few hours of sampling and occurs during a more limited time (e.g., one to three days). Guidance on point-source sampling schedules is presented in the following:

U.S. EPA. November 1985. Practical Guide - Trial Burns for Hazardous Waste Incinerators. NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.

U.S. EPA. Code of Federal Regulations. 40 CFR Part 60: Appendix A: Reference Methods. Office of the Federal Register. Washington, D.C. 20640.

U.S. EPA. 1978. Stack Sampling Technial Information, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042a,b,c. NTIS PB 80-161672, 80-161680, 80-161698. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. February 1985. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. March 1984. Protocol for the Collection and Analysis of Volatile POHCs Using VOST. EPA-600/8-84-007. NTIS PB 84-170042. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. February 1984. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA-600/8-84-002. NTIS PB 84-155845. Washington, D.C. 20460.

U.S. EPA. 1981. Source Sampling and Analysis of Gaseous Pollutants. EPA- APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, N.C. 27711.

U.S. EPA. 1979. Source Sampling for Particulate Pollutants. EPA-APTI Course Manual 450. NTIS PB 80-188840, 80-182439, 80-174360. Air Pollution Control Institute. Research Triangle Park, N.C. 27711.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. Office of Solid Waste. EPA/SW-846. GPO No. 955-001-00000-1. Washington, D.C. 20460.

Guidance on area source emission rate monitoring is provided in the following:

U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide. EPA/600/8-86/008. NTIS PB86-223161. Environmental Monitoring Systems Laboratory. Las Vegas, NV 89114.

12.4.4.3 Subsequent Monitoring

Subsequent monitoring may be necessary if initial monitoring data were not sufficient to estimate "reasonable worst case" long-term concentrations at actual offsite receptors. Additional monitoring may also be necessary to evaluate air concentration levels subsequent to the implementation of corrective measures.

The same schedule specified for the initial monitoring phase is also applicable to subsequent monitoring. However, when evaluating the results of subsequent monitoring and comparing them to previously collected data, potential differences in emission/dispersion conditions and other data representativeness factors should be accounted for.

12.4.5 Monitoring Approach

Use of an upwind/downwind network of monitors or sample collection devices is the primary approach recommended to determine ambient and background concentrations of the constituents of concern. Dispersion models may also be used for many applications to extrapolate ambient data collected at the facility to actual offsite receptor locations, if it is not feasible to collect offsite monitoring data. Alternatively, for certain situations emission monitoring can be performed at the source of the release to determine the rate of the release, with downwind concentrations estimated using mathematical dispersion models.

Emission monitoring in conjunction with dispersion modeling may be an effective alternative for the following cases:

- Meteorological conditions (e.g., constant high winds) or high background concentrations of contaminants prevent viable measurement of the release;
- The source can be localized sufficiently to allow representative collection of emission samples (e.g., landfill vents, incinerator stacks, etc.); and
- Expected ambient constituent concentrations from an area source are expected to be below analytical detection limits but may still be of concern. In this case, isolation flux chamber sampling at the unit may be applied. This device is discussed below and in Appendix E.

A summary of applicable air monitoring strategies related to source type is presented in Table 12-8.

12.4.5.1 Ambient Air Monitoring

Upwind/downwind ambient air monitoring networks provide concentrations of the constituents of concern at the point of monitoring, whether that be at the unit boundary, facility property boundary, or at a receptor point. The upwind/downwind approach involves the placement of monitors or sample collection devices at various points around the unit of concern. Each air sample

TABLE 12-8
APPLICABLE AIR SAMPLING STRATEGIES BY SOURCE TYPES

Unit Type/Expected Emission	Air Sampling Strategy		
	Ambient Monitoring	Emissions Monitoring	
		Source Sampling	Isolation Flux Chambers
AREA SOURCES WITH LIQUID SURFACES			
Surface Impoundments			
Vapor Phase	X		X
Particulates	X		
Open Roof Storage/Treatment Tanks			
Vapor Phase	X	X	X
AREA SOURCES WITH SOLID SURFACES			
Waste Piles			
Vapor Phase	X		X
Particulates	X		
Landfill Surface			
Vapor Phase	X		X
Particulates	X		
Land Treatment			
Vapor Phase	X		X
Particulates	X		
POINT SOURCES			
Vents from container Handling Units			
Vapor Phase	X	X	
Landfill Vents			
Vapor Phase	X	X	X
Storage/Treatment Tank Vents			
Vapor Phase	X	X	
Incinerators			
Vapor Phase	X	X	
Particulates	X	X	

collected is classified as upwind or downwind based on the wind conditions for the sampling period. Downwind concentrations are compared to those measured at upwind points to determine the relative contribution of the unit to ambient concentrations of toxic compounds. This is generally accomplished by subtracting the upwind concentration (which represents background conditions) from the concurrent downwind concentrations. Applicable field methods for ambient air monitoring are discussed in Section 12.6. Ambient downwind concentrations at the facility can be extrapolated to actual offsite receptor locations by using dispersion modeling results. As discussed previously, this may be necessary if practical limitations (e.g., potential for vandalism, site access limitations) preclude the collection of offsite air monitoring data.

12.4.5.2 Source Emissions Monitoring

Monitoring at the source to measure a rate of emission for the constituents of concern may, in some cases, offer a more practical approach to characterizing air emissions. Using this technique, the emission rate is then input into a mathematical dispersion model for estimation of downwind concentrations. One distinct disadvantage of this approach is that the value achieved for a concentration at a downwind point is not a measurement, but an estimation modeled from a series of input parameters such as wind speed and emission rate. However, the approach does have advantages in that interference from sources close to the unit are eliminated because the source is isolated from the ambient atmosphere for monitoring purposes, and in that source monitoring techniques do not require the level of sensitivity required by ambient monitors. Concentrations of airborne constituents at the source are generally higher than at downwind locations due to the lack of dispersion of the constituent over a wide area. The concentrations expected in ambient air (generally part-per-billion levels) may be at or near the limit of detectability of the methods used. Methods for source emissions monitoring for various constituent classes are discussed in Section 12.6.

Area sources (such as landfills, land treatment units, and surface impoundments) can be monitored using the isolation flux chamber approach. This method involves isolating a small area of contamination under a flux chamber, and passing a known amount of a zero hydrocarbon carrier gas through the chamber, thereby picking up any volatile emissions in the effluent gas stream from the flux chamber. Samples of this effluent stream are collected in inert sampling containers, usually stainless steel canisters under vacuum, and removed to the laboratory for subsequent analysis. The analytical results of the identified analytes can be converted through a series of calculations to direct emission rates from the source. These emission rates can be used to evaluate downwind concentrations by application of dispersion models. More information on use of the isolation flux chamber is provided in Appendix E and in the following reference:

> U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber User's Guide. EPA/600/8- 86/008. NTIS PB 86-223161. Washington, D.C. 20460.

Some area source units may not be amenable to the source sampling approach, however. A unit in which the source cannot be isolated and viable measurements taken of the parameters of concern is one example. This includes active areas of landfills and land-treatment areas, as well as aerated surface impoundments. Also, area sources in which particulate emissions are of concern cannot be measured using an isolation flux chamber due to technical limitations in the technique. For these applications, only an upwind/downwind monitoring approach should be used.

12.4.6 Monitoring Locations

As with other factors associated with air monitoring, siting of the monitors should reflect the primary objective of the monitoring to characterize concentrations at existing offsite receptors. This section discusses monitoring locations for both upwind/downwind approaches and source monitoring techniques in relation to the objectives of both initial and subsequent monitoring.

12.4.6.1 Upwind/Downwind Monitoring Locations

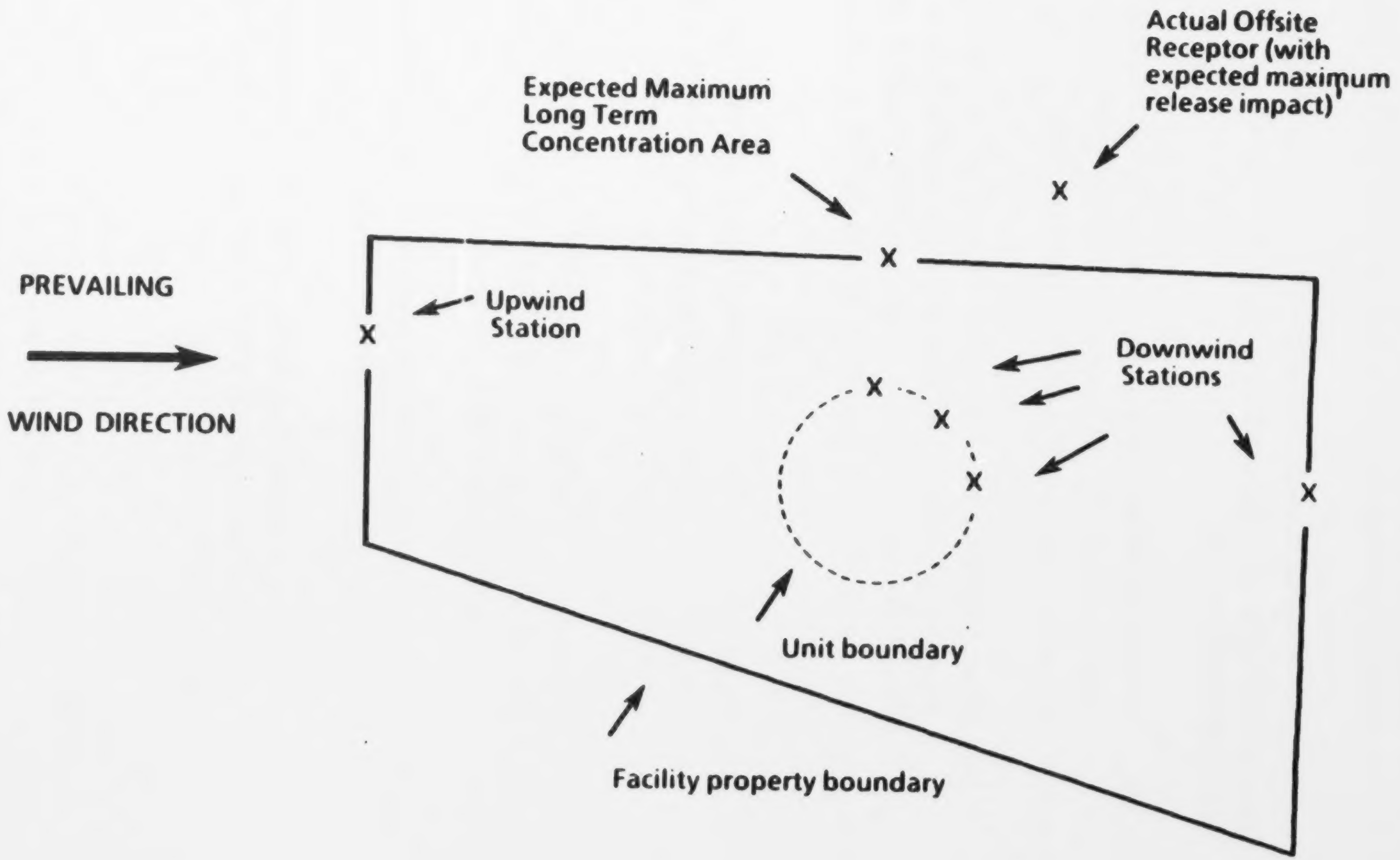
The ambient air monitoring network design should provide adequate coverage to characterize both upwind (background) and downwind concentrations. Therefore, four air monitoring zones are generally necessary for initial monitoring. Multiple monitoring stations per zone will frequently be required to adequately characterize the release. An upwind zone is used to define background concentration levels. Downwind zones at the unit boundary and at or beyond the facility property boundary are used to define potential offsite receptor exposure.

The location of air monitoring stations should be based on local wind patterns. Air monitoring stations should be placed at the following strategic locations, as illustrated in Figure 12-6:

- Upwind (based on the expected prevailing wind flow during the 90-day monitoring period) of the unit and near the facility property boundary to characterize background air concentration levels.
- Downwind (based on the expected prevailing wind flow during the 90-day monitoring period) at the unit boundary plus stations at adjacent sectors also at the unit boundary (the seperation distance of air monitoring stations at the unit boundary should be 30° or 50 feet, whichever is greater).
- Downwind (based on the expected prevailing wind flow during the 90-day monitoring period) at the facility property boundary (this station may not be required if the site perimeter is within 100 m of the unit boundary).
- Downwind (at the area expected to have the highest average concentration levels during the 90-day monitoring period) just beyond the facility property boundary.
- Downwind at actual offsite receptor locations (if practical) expected to have the greatest impact from the release.
- Additional locations at complex terrain and coastal sites associated with pronounced secondary air flow paths (e.g., downwind of the unit near the facility property boundary for both primary daytime and nighttime flow paths).

The above locations should be selected prior to initial monitoring based on the onsite meteorological survey and on evaluation of available representative offsite meterological data. This analysis should provide an estimate of expected wind

FIGURE 12-6. EXAMPLE AIR MONITORING NETWORK.


Actual Offsite Receptor (with expected maximum release impact)
Expected Maximum Long Term Concentration Area
PREVAILING
WIND DIRECTION
Upwind Station
Downwind Stations
Unit boundary
Facility property boundary

conditions during the 90-day initial monitoring period. If sufficient representative data are available, dispersion modeling can be used to identify the area of maximum long term concentration levels at the facility property boundary and at actual offsite receptors. If not, the facility property boundary sector nearest to the unit of concern should be selected for initial monitoring.

The network design defined above will provide an adequate basis to define long-term concentrations based on continuous monitoring during the 90-day initial monitoring period. The monitoring stations at the unit boundary should increase the potential for release detection. The facility property boundary air monitoring stations should provide data (with the aid of dispersion modeling, if appropriate) to characterize offsite concentrations.

Ambient monitoring at offsite receptors may be impractical in many cases, because analytical detection limits may not be low enough at offsite receptor locations to measure the release. Also, a 90-day offsite monitoring program can be problematic. Factors such as vandalism, erroneous readings due to public tampering with the equipment, public relations problems in setting up the equipment, and legal access problems may preclude the use of offsite air monitoring stations. For these cases, dispersion models may be used to extrapolate monitoring data collected at the facility to actual offsite receptor locations.

If subsequent monitoring is required, a similar network design to that illustrated in Figure 12-6 will generally be appropriate. Evaluation of the meteorological monitoring data collected during the initial phase should provide an improved basis to identify local prevailing and diurnal wind flow paths. Also, the site meteorological data will provide dispersion modeling input. These modeling results should provide dilution patterns that can be used to identify areas with expected relatively high concentration levels. However, these results should account for seasonal meteorological differences between initial and subsequent monitoring periods.

Wind-directionally controlled air monitoring stations can also be used at sites with highly variable wind directions. These wind-directionally controlled stations should be collocated with the fixed monitoring stations. This approach facilitates determination of the unit source contribution to total constituent levels in the local area. These automated stations will only sample for a user-defined range of wind directions (e.g., downwind stations would only sample if winds were blowing from the source towards the station.) Interpretation of results from wind-directionally controlled air monitoring stations should account for the lower sampling volumes (and therefore, the possibility that not enough sample would be collected for analysis) generally associated with this approach.

The inlet exposure height of the air monitors should be 2 to 15 m to be representative of potential inhalation exposure but not unduly biased by road dust and natural wind erosion phenomena. Further guidance on air monitoring network design and station exposure criteria (e.g., sampling height and proximity to structures and air emission sources) is provided in the following reference:

> U.S. EPA. September 1984. Network Design and Site Exposure Criteria for Selected Non-criteria Air Pollutants. EPA-450/4-84-022. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

The above referenced document recommends the use of dispersion models to identify potential relatively high concentration areas as a basis for network design. This topic is also discussed in the following document:

> U.S. EPA. July 1986. Guidelines on Air Qualilty Models (Revised). EPA- 450/2-78-027R. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

Uniformity among the sampling sites should be achieved to the greatest degree possible. Descriptions should be prepared for all sampling sites. The description should include the type of ground surface, and the direction, distance, and approximate height with respect to the source of the release. Location should also be described on a facility map.

12.4.6.2 Stack/Vent Emission Monitoring

Point source measurements should be taken in the vent near the point of release. If warranted, an upwind/downwind monitoring network can be used to supplement the release rate data. Both the VOST and Modified Method 5 methodologies describe the exact placement in the stack for the sampler inlet. (See Section 12.6.3).

12.4.6.3 Isolation Flux Chambers

Monitor placement using flux chambers (discussed earlier) is similar to conducting a characterization of any area source. Section 3 of this guidance discusses establishment of a grid network for sampling. Such a grid should be established for an area source, with sampling points established within the grids, as appropriate. It is suggested that a minimum of six points be chosen for each monitoring effort. Once these areas are sampled, the results can be averaged to provide an overall compound specific emission rate for the plot. Additional guidance on the use of isolation flux chambers is presented in Appendix E.

12.5 Data Presentation

As discussed in Section 5, progress reports will be required by the regulatory agency at periodic intervals during the investigation. The following data presentation formats are suggested for the various phases of the air investigation in order to adequately characterize concentrations at actual offsite receptors.

12.5.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

- Tables of waste constituents and concentrations;
- Tables of relevant physical/chemical properties for potential air emission constituents;
- Tables and narratives describing unit dimensions and special operating conditions and operating schedules concurrent with the air monitoring program;
- Narrative description of unit operations; and

- Identification of "reasonable worst case" emissions conditions that occurred during the monitoring period.

12.5.2 Environmental Setting Characterization

Environmental characteristics should be presented as follows:

- Climate (historical summaries from available onsite and offsite sources):
  - Annual and monthly or seasonal wind roses;
  - Annual and monthly or seasonal tabular summaries of mean wind speeds and atmospheric stability distributions; and
  - Annual and monthly or seasonal tabular summaries of temperature and precipitation.
- Meteorological survey results:
  - Hourly listing of all meteorological parameters for the entire monitoring period;
  - Daytime wind rose (at coastal or complex terrain sites);
  - Nightime wind rose (at coastal or complex terrain sites);
  - Summary wind rose for all hours;
  - Summary of dispersion conditions for the monitoring period (joint frequency distributions of wind direction versus wind speed category and stability class frequencies); and
  - Tabular summaries of means and extremes for temperature and other meteorological parameters.
- Definition of soil conditions (if appropriate):

  - Narrative of soil characteristics (e.g., temperature, porosity and organic matter content); and

  - Characterization of soil contamination conditions (e.g., in land treatment units, etc,).

- Definition of site-specific terrain and nearby receptors:

  - Topographic map of the site area with identification of the units, meteorological and air monitoring stations, and facility property boundary;

  - Topographic map of 10-kilometers radius from site (U.S. Geological Survey 7.5 minute quandrangle sheets are acceptable); and

  - Maps which indicate location of nearest residence for each of sixteen 22.5 degree sectors which correspond to major compass points (e.g., north, north-northwest, etc.), nearest population centers and sensitive receptors (e.g., schools, hospitals and nursing homes).

- Maps showing the topography of the area, location of the unit(s) of concern, and the location of meteorological monitoring equipment.

- A narrative description of the meteorological conditions during the air sampling periods, including qualitative descriptions of weather events and precipitation which are needed for data interpretation.

12.5.3 Characterization of the Release

Characteristics of the release should be presented as follows:

- Screening sampling:

  - Identification of sampling and analytical methodology;

  - Map which identifies sampling locations;

  - Listing of measured concentrations indicating collection time period and locations;

  - Prioritization of units as air release sources which warrant monitoring based on screening results;

  - Discussion of QA/QC measures and results; and

  - Listing and discussion of meteorological data during the sampling period.

- Initial and subsequent monitoring results:

  - Identification of monitoring constituents;

  - Discussion of sampling and analytical methodology as well as equipment and specifications;

  - Identification of monitoring zones as defined in Section 12.4.6.1;

  - Map which identifies monitoring locations relative to units;

  - Discussion of QA/QC measures and results;

  - Listing of concentrations measured by station and monitoring period indicating concentrations of all constituents for which monitoring was conducted. Listings should indicate detection limits if a constituent is not detected;

  - Summary tables of concentration measured indicating maximum and mean concentration values for each monitoring station;

- Discussion of meteorological station locations selection, sensor height, local terrain, nearby obstructions and equipment specifications;

- Listing of all meteorological parameters concurrent with the air sampling periods;

- Daytime wind rose (only for coastal or complex terrain areas);

- Nightime wind rose (only for coastal or complex terrain areas);

- Summary wind rose based on all wind direction observations for the sampling period;

- Summary of dispersion conditions for the sampling period (joint frequency distributions of wind direction versus wind speed category and stability class frequences based on guidance presented in Guidelines on Air Quality Models, U.S. EPA, July 1986);

- Tabular summaries of means and extremes for temperature and other meteorological parameters;

- A narrative discussion of sampling results, indicating problems encountered, relationship of the sampling activity to unit operating conditions and meteorological conditions, sampling periods and times, background levels and identification of other air emission sources and interferences which may complicate data interpretation;

- Presentation and discussion of models used (if any), modeling input data and modeling output data (e.g., dilution or dispersion patterns based on modeling results); and

- Concentrations based on monitoring and/or modeling for actual offsite receptor locations.

Interpretation of air monitoring results should also account for additional factors such as complex terrain, variable winds, multiple contaminant sources and intermittent or irregular releases. The key to data interpretation for these cases is to evaluate monitoring results as a function of wind direction.

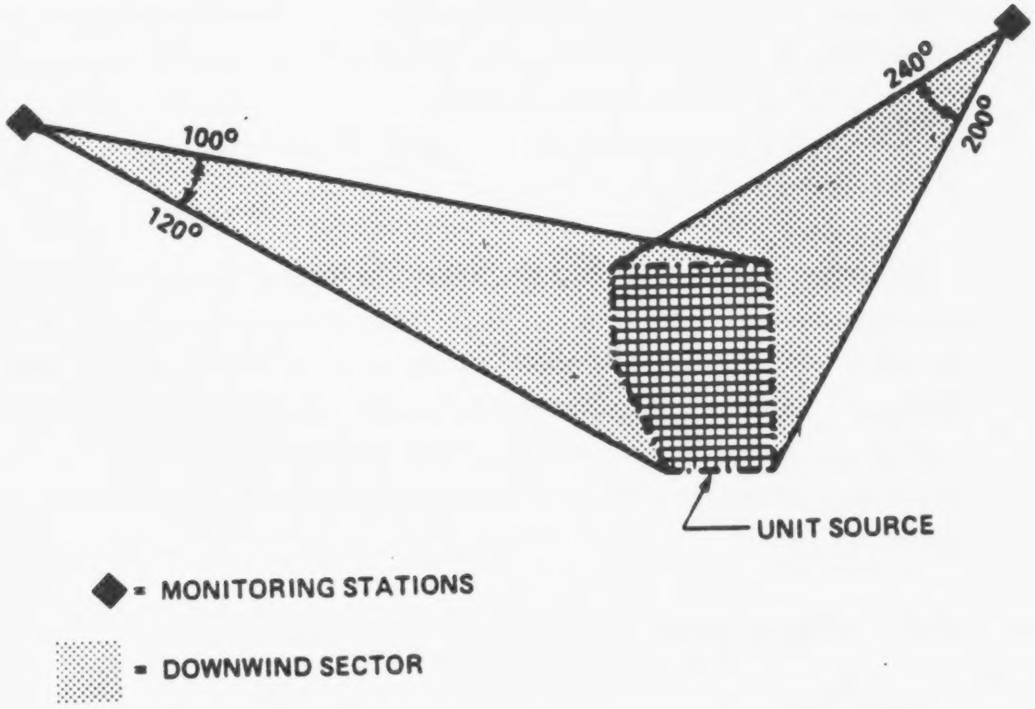
Terrain factors can alter wind flow trajectories especially during stable nightime conditions. Therefore, straightline wind trajectories may not occur during these conditions if there is intervening terrain between the source and the air monitoring station. For these cases wind flows will be directed around large obstacles (such as hills) or channeled (for flows within valleys). Therefore, it is necessary to determine the representativeness of the data from the meteorological stations as a function of wind direction, wind speed and stability conditions. Based on this assessment, and results from the meteorological survey, upwind and downwind sectors (i.e., a range of wind direction as measured at the meteorological station) should be defined for each air monitoring station to aid in data interpretation. Figure 12-7 illustrates an example which classifies a range of wind directions during which the air monitoring stations will be downwind of an air emission source. Therefore, concentrations measured during upwind conditions can be used to characterize background conditions and concentrations measured during downwind conditions can be used to evaluate the air-quality impact of the release.

Complex terrain sites and coastal sites frequently have very pronounced diurnal wind patterns. Therefore, as previously discussed, the air monitoring network at these sites may involve coverage for multiple wind direction sectors and use of wind-directionally controlled air samplers. This monitoring approach is also appropriate for sites with highly variable wind conditions. Comparing results from two collocated air monitoring stations (i.e., one station which samples continuously and a second station at the same location which is wind-directionally controlled on an automated basis), facilitates determination of source contributions to ambient air concentrations.

Comparison of results from collocated (continuous versus wind-directionally controlled) air monitoring stations can also be used to assist in data interpretation at sites with multiple air emissions sources or with intermittent/irregular releases. For some situations, the consistent appearance of certain air emission constituents can be used to "fingerprint" the source. Therefore, the air monitoring results can

Figure 12-7

EXAMPLE OF DOWNWIND EXPOSURES AT AIR MONITORING STATIONS


100°
120°
240°
200°
UNIT SOURCE
◆ = MONITORING STATIONS
▨ = DOWNWIND SECTOR

be classified based on these "fingerprint" patterns. These results can then be summarized as two seperate data sets to assess background versus source contributions to ambient concentrations.

The use of collocated (continuous and wind-directionally controlled) air monitoring stations is a preferred approach to data interpretation for complex terrain, variable wind, multiple source and intermittent release sites. An alternative data interpretation approach involves reviewing the hourly meteorological data for each air sampling period. Based on this review, the results from each sampling period (generally a 24-hour period) for each station are classified in terms of downwind frequency. The downwind frequency is defined as the number of hours winds were blowing from the source towards the air monitoring station divided by the total number of hours in the sampling period. These data can then be processed (by plotting scattergrams) to determine the relationship of downwind frequency to measured concentrations.

Data interpretation should also take into account the potential for deposition, degradation and transformation of the monitoring constituents. These mechanisms can affect ambient concentrations as well as air sample chemistry (during storage). Therefore, standard technical references on chemical properties, as well as the monitoring guidance previously cited, should be consulted to determine the importance of degradation and transformation for the monitoring constituents of concern.

12.6 Field Methods

This section describes field methods which can be used during initial or subsequent monitoring phases. Methods are classified according to source type and area. Guidance on meteorological monitoring methods is also provided in this section.

12.6.1 Meteorological Monitoring

Meteorological monitoring generally should employ a 10-meter tower equipped with wind direction, wind speed, temperature and atmospheric stability instrumentation. Wind direction and wind speed monitors should exhibit a starting threshold of less than 0.5 meter per second (m/s.). Wind speed monitors should be accurate above the starting threshold to within 0.25 m/s at speeds less than or equal to 5 m/s. At higher speeds the error should not exceed 5 percent of the wind speed. Wind direction monitors errors should not exeed 5 degrees. Errors in temperature should not exceed 0.5°C during normal operating conditions.

The meteorological station should be installed at a location which is representative of overall site terrain and wind conditions. Multiple meteorological station locations may be required at coastal and complex terrain sites.

Additional guidance on equipment performance specifications, station location, sensor exposure criteria, and field methods for meteorological monitoring are provided in the following references:

U.S. EPA. February 1983. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV, Meteorological Measurement. EPA-600-4-82-060. NTIS PB 254-658/8. Office of Research and Development, Research Triangle Park, N.C. 27711.

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EP-450/2-78-027R. NTIS PB 288-783. Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711.

12.6.2 Ambient Air Monitoring

Selection of methods for monitoring ambient contaminants should consider a number of factors, including the compounds to be detected, the purpose of the method (e.g., screening or quantification), the detection limits, and sampling rates and duration required for the investigation.

Organic and inorganic constituents require different analytical methods. Within these two groups, different methods may also be required depending on the constituent and its physical/chemical properties. Another condition that affects the choice of monitoring technique is whether the compound is primarily in the gaseous phase or is found adsorbed to solid particles or aerosols.

Screening for the presence of ambient air constituents involves techniques and equipment that are rapid, portable, and can provide "real-time" monitoring data. Air contamination screening will generally be used to confirm the presence of a release, or to establish the extent of contamination during the screening phase of the investigation. Quantification of individual components is not as important during screening as during initial and subsequent monitoring, however the technique must have sufficient specificity to account for the hazardous constituents of concern from potential interferences, even when the latter are present in higher concentrations. Detection limits for screening devices are often higher than for quantitative methods.

Laboratory analytical techniques must provide positive identification of the components, and accurate and precise measurement of concentrations. This generally means that preconcentration and/or storage of air samples will be required. Therefore, methods chosen for quantification usually involve a longer analytical time-period, more sophisticated equipment, and more rigorous quality assurance procedures.

The following list of references provides guidance on ambient air monitoring methodologies:

U.S. EPA. June 1983. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air. NTIS PB 83-239020. EPA-600/4-83-027. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. April 1984. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. EPA-600/4-84-041. Office of Research and Development. Research Triangle Park, NC 27711.

NIOSH. February 1984. NIOSH Manual of Analytical Methods. NTIS PB 85-179018. National Institute for Occupational Safety and Health. Cincinnati, OH.

U.S. EPA. September 1983. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II, Available Sampling Methods. NTIS PB 84-126929. EPA-600/4-83-040. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. September 1983. Characterization of Hazardous Waste Sites - A Methods Manual: Volume III, Available Laboratory Analytical Methods. EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste, Washington, D.C. 20460.

U.S. EPA. September, 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA SW-846. GPO No 955-001-00000-1. Office of Solid Waste, Washington, D.C. 20460.

ASTM. 1982. Toxic Materials In the Atmosphere. ASTM, STP 786. Philadelphia, PA.

ASTM. 1980. Sampling and Analysis of Toxic Organics in the Atmosphere. ASTM, STP 721. Philadelphia, PA.

ASTM. 1974. Instrumentation for Monitoring Air Quality. ASTM, STP 555. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association. Cincinnati, OH.

ACGIH. 1983. Air Sampling Instruments for Evaluation of Atmospheric Contaminants. American Conference of Governmental Industrial Hygienists. Washington, D.C.

12.6.2.1 Screening Methods

Screening techniques for vapor-phase constituents fall into two main categories. (1) organic and non-organic compound-specific indicators, and (2) general organic detectors. Table 12-9 presents a summary of commercially available screening methods for these compounds.

TABLE 12-9
TYPICAL COMMERCIALLY AVAILABLE SCREENING TECHNIQUES FOR ORGANICS IN AIR (FROM RIGGIN, 1983)

Technique	Manufacturers	Compounds Detected	Approximate Detection Limit	Comments
Gas Detection Tubes	Draeger Matheson Kitagawa	Various organics and inorganics	0.1 to 1 ppmv	Sensitivity and selectivity highly dependent on component of interest.
Continuous Flow Colorimeter	CEA Instruments, Inc.	Acrylonitrile, Formaldehyde, Phosgene, and various organics	0.05 to 0.5 ppmv	Sensitivity and selectivity similar to detector tubes.
Colorimetric Tape Monitor	KHDA Scientific	Toluene, diisocyanate, dinitro toluene, phosgene, and various inorganics	0.05-0.5 ppmv	Same as above.
Infrared Analysis	Foxboro/Wilkes	Most organics	1-10 ppmv	Some inorganic gases (H_20, CO) will be detected and therefore are potential interferences.
FID (Total Hydrocarbon Analyzer)	Beckman HSA, Inc. AID, Inc.	Most organics	0.5 ppmv	Responds uniformly to most organic compounds on a carbon basis.
GC/FID (portable)	Foxboro/Century AID, Inc.	Same as above except that polar compounds may not elute from the column.	0.5 ppmv	Qualitative as well as quantitative information obtained.
PID and GC/PID (portable)	HNU, Inc. AID, Inc. Photovac, Inc.	Most organic compounds can be detected with the exception of methane	0.1 to 100 ppbv	Selectivity can be adjusted by selection of lamp energy. Aromatics most readily detected.
GC/ECD (portable)	AID, Inc.	Halogenated and nitro-substituted compounds	0.1 to 100 ppbv	Response varies widely from compound to compound.
GC/FPD (portable)	AID, Inc.	Sulfur or phosphorus-containing compounds	10-100 ppbv	Both inorganic and organic sulfur or phosphorus compounds will be detected.
Chemiluminescent Nitrogen Detector	Antek, Inc.	Nitrogen-containing compounds	0.1 ppmv (as N)	Inorganic nitrogen compounds will interfere.

Indicator tubes and other colorimetric methods--Indicator tubes, also known as gas detector or Draeger tubes, are small glass tubes filled with a reagent-coated material which changes color when exposed to a particular chemical. Air is pulled through the tube with a low-volume pump. Tubes are available for 40 organic gases, and for 8 hour or 15 minute exposure periods. Indicator tubes were designed for use in occupational settings, where high levels of relatively pure gases are likely to occur. Therefore, they have only limited usefulness for ambient air sampling, where part-per-billion levels are often of concern. However, because they are covenient to use and available for a wide range of compounds, detector tubes may be useful in some screening/sampling situations.

Other colorimetric methods, such as continuous flow and tape monitor techniques, were developed to provide real-time monitoring capability with indicator methods. The disadvantages of these systems are similar to those of indicator tubes.

Instrumental detection screening methods--More commonly used for volatile organic surveys, are portable instrumental detection methods including flame ionization detectors (FID), photoionization detectors (PID), electron capture detectors (ECD) and infrared detectors (ID). Also in use are detectors that respond to specific chemical classes such as sulfur- and nitrogen- containing organics. These instruments are used to indicate levels of total organic vapors and for identification of "hot zones" downwind of the release source(s). They can be used as real-time non-specific monitors or, by adding a gas chromatograph, can provide concentration estimates and tentative identification of pollutants.

Of the available detectors, those that are the most applicable to an RFI are the FID and PID. Table 12-10 summarizes four instruments (two FID and two PID versions) which are adequate for the purposes of the screening phase.

Flame Ionization Detectors--The Century OVA 100 series and AID Model 550 utilize a FID to determine the presence of vapor phase organics. The detector responds to the total of all organics present in the air at any given moment. Flame ionization detectors will respond to most organics, but are most sensitive to hydrocarbons, (i.e., those chemicals which contain only carbon and hydrogen

Table 12-10

Summary of Selected Onsite Organic Screening Methodologies

Instrument or detector	Measurable parameters	Low range of detection	Comments
Century Series 100 or AID Model 550 (survey mode)	Volatile organic species	Low ppm	Uses Flame Ionization Detector (FID)
HNU Model PI-101	Volatile organic species	Low ppm	Photo-ionization (PI) detector-provides especially good sensitivity to low molecular weight aromatic compounds (i.e., benzene, toluene)
Century Systems OVA-128 (GC mode)	Volatile organic species	Low ppm	Uses GC column for possible specific compound identification
Photo Vac 10A10	Volatile organic species	Low ppm	Uses PI detector. Especially sensitive to aromatic species. May be used for compound identification if interferences are not present

molecules such as benzene and propane). FIDs are somewhat less sensitive to compounds containing chlorine, nitrogen, oxygen, and sulfur molecules. The response is calibrated against a reference gas, usually methane. FID response is often termed "total hydrocarbons"; however, this is misleading because particulate hydrocarbons are not detected. FID detection without gas chromatography is not useful for quantification of individual compounds, but provides a useful tool for general assessment purposes. Detection limits using a FID detector alone are about 1 ppm. Addition of a gas chromatograph (GC) lowers the detection limit to ppb levels, but increases the analysis time significantly.

Photoionization Detectors--Portable photoionization detectors such as the HNU Model PI-101 and the Photovac 10A10 operate by applying UV ionizing radiation to the contaminant molecules. Some selectivity over the types of organic compounds detected can be obtained by varying energy of the ionizing beam. In the screening mode this feature can be used to distinguish between aliphatic and aromatic hydrocarbons and to exclude background gases from the instrument's response. The HNU and Photovac can be used either in the survey mode (PID only), or with GC. Sensitivity with PID alone is about 1 ppm, but can go down to as low as 0.1 ppb when a GC is used for preconcentration.

PI and FI detectors used in the GC mode can be used for semiquantitative analysis of compounds in ambient air. However, in areas where numerous contaminants are present, identification of peaks in a complex matrix may be tentative at best.

Another method which can be used as a survey technique is mobile mass spectrometry. Ambient air is drawn through a probe directly into the instrument, which is usually mounted in a van. Particularly in the MS/MS configuration this is a powerful technique which can provide positive identification and semiquantitative measurement of an extremely wide range of organic and inorganic gaseous contaminants.

12.6.2.2 Quantiative Methods

Laboratory analysis of hazardous constituents in ambient air includes the following standard steps:

- Preconcentration of organics (as necessary to achieve detection limit goals);

- Transfer to a gas chromatograph or HPLC (High Pressure Liquid Chromatography); and

- Quantification and/or identification with a detector.

Broad-spectrum methods applicable to most common air contaminants are discussed below.

12.6.2.2.1 Monitoring Organic Compounds in Ambient Air

Due to the large number of organic compounds that may be present in ambient air, and their wide range in chemical and physical properties, no single monitoring technique is applicable to all organic air contaminants. Numerous techniques have been developed, and continue to be developed, to monitor for specific compound classes, individual chemicals, or to address a wide range of hazardous contaminants. This last approach may be the most efficient approach to monitoring at units where a wide range of chemicals are likely to be present. Therefore, methods that apply to a broad range of compounds are recommended. In cases where specific compounds of concern are not adequately measured by broad-spectrum methods, compound-specific techniques are described or referenced.

12.6.2.2.1.1 Vapor-Phase Organics

The majority of hazardous constituents of concern can be classified as gaseous or (vapor-phase) organics. These constituents include most petroleum-related hydrocarbons, organic solvents, and many pesticides, and other semivolatile organic compounds. Methods to monitor these compounds generally include on-site analysis (making use of onsite concentration techniques, where necessary), or require storage in a tightly sealed non-reactive container.

Techniques for volatile and semivolatile organics measurement include:

- Adsorption of the sample on a solid sorbent with subsequent desorption (thermal or chemical), followed by gas chromatographic analysis using a variety of detectors.
- Collection of whole air (grab) samples in an evacuated flask or in Tedlar or Teflon bags, with direct injection of the sample into a GC using high sensitivity and/or constituent-specific detectors. This analysis may or may not be preceded by a preconcentration step.
- Cryogenic trapping of samples in the field with subsequent instrumental analysis.
- Bubbling ambient air through a liquid-filled impinger, containing a chemical that will absorb or react with specific compounds to form more stable products for GC analysis.
- Direct introduction of the air into a MS/MS or other detector.

Tables 12-11 (A and B), 12-12, and 12-13 summarize sampling and analytical techniques that are applicable to a wide range of vapor phase organics, have been widely tested and validated in the literature, and make use of equipment that is readily available. A discussion of general types of techniques is given below.

Sorbent techniques--A very common technique used to sample vapor-phase organics involves sorption onto a solid medium. Methods of this type usually employ a low- or high-volume pump to pull air through a glass tube containing the sorbent material. Organic compounds are trapped (removed from the air) by chemical attraction to the surface of the adsorbent material. After a predetermined volume of air has been pulled through the trap, the tube is capped and returned to the laboratory for analysis. Adsorbed organics are then thermally or chemically desorbed from the trap prior to GC or GC/MS analysis.

TABLE 12-11A. SUMMARY OF CANDIDATE METHODOLOGIES FOR QUANTIFICATION OF VAPOR PHASE ORGANICS

Collection Technique	Analytical Technique	Applicability (See Table 12-11B)	Positive Aspects	Negative Aspects
I. Sorption onto Tenax-GC or carbon molecular sieve packed cartridges using low-volume pump	Thermal Desorption into GC or GC/MS	I	• adequate QA/QC data base • widely used on investigations around uncontrolled waste sites • wide range of applicability • μ/m³ detection limits • practicality for field use	• possibility of contamination • artifact formation problems • rigorous cleanup needed • no possibility of multiple analysis • low breakthrough volumes for some compounds
II. Sorption onto charcoal packed cartridges using low-volume pump	Resorption with solvent-analysis by GC or GC/MS	II	• large data base for various compounds • wide use in industrial applications • practicality for field use	• problems with irreversible adsorption of some compounds • high (mg/m³) detection limits • artifact formation problems • high humidity reduces retention efficiency
III. Sorption onto polyurethane foam (PUF) using low-volume or high-volume pump	Solvent extraction of PUF; analysis by GC/MS	I, II, III	• wide range of applicability • easy to preclean and extract • very low blanks • excellent collection and retention efficiencies • reusable up to 10 times	• possibility of contamination • losses of more volatile compounds may occur during storage
IV. Sorption on passive dosimeters using Tenax or charcoal as adsorbing medium	Analysis by chemical or thermal desorption following by GC or GC/MS	I or II	• samplers are small, portable, require no pumps • makes use of analytical procedures of known precision and accuracy for a broad range of compounds • pg/m³	• problems associated with sampling using sorbents (see #1 and 11) are present • uncertainty in volume of air sampled makes concentration calculations difficult • requires minimum external air flow rate

TABLE 12-11A (Continued)

Collection Technique	Analytical Technique	Applicability (see Table 12-11B)	Positive Aspects	Negative Aspects
V. Cryogenic trapping of analytes in the field	Desorption into GC	II, III	• applicable to a wide range of compounds • artifact formation minimized • low blanks	• requires field use of liquid nitrogen or oxygen • sample is totally used in one analysis - no reanalysis possible • samplers easily clogged with water vapor • no large data base on precision or recoveries
VI. Whole air sample taken in glass or stainless steel bottles	Cryogenic trapping or direct injection into GC or GC/MS (onsite or laboratory analysis)	II, III	• useful for grab sampling • large data base • excellent long-term storage • wide applicability • allows multiple analyses	• difficult to obtain integrated samples • low sensitivity of preconcentration is not used
VII. Whole air sample taken in Tedlar^K Bag	Cryogenic trapping or direct injection into GC or GC/MS (onsite or laboratory)	II, III	• grab or integrated sampling • wide applicability • allows multiple analyses	• long-term stability uncertain • low sensitivity if preconcentration is not used • adequate cleaning of containers between samples may be difficult
IX. Denitrophenyl - hydrazine Liquid Impinger Sampling using a Low-Volume Pump	HPLC/UV analysis	IV	• specific to aldehydes and ketones • good stability for derivatized compounds • low deteciton limits	• fragile equipment • sensitivity limited by reagent impurities • problems with solvent evaporation when long-term sampling is performed
X. Direct introduction by probe	Mobile MS/MS	I, II, III, IV	• immediate results • field identification of air contaminants • allows "real-time" monitoring • widest applicability of any analytical method	• high instrument cost ($250K) • requires highly trained oeprators • grab samples only • no large data base on precision or accuracy

TABLE 12-11B. LIST OF COMPOUND CLASSES REFERENCED IN TABLE 12-13A

Category	Types of Compound
I	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80 to 200°C.
II	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15 to + 120°C.
III	Semivolatile organic chemicals (e.g., organochlorine pesticides and PCBs).
IV	Aldehydes and ketones.

TABLE 12-12. SAMPLING AND ANALYSIS TECHNIQUES APPLICABLE TO VAPOR PHASE ORGANICS

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Acetophenone	X	X						
Acrolein	X					X		
Acrylonitrile	X		X	X				
Aniline	X			X			2002	
Arsenic and compounds							7900	Solid, use Std. Hi-Vol
Benzene	X	X	X	X				
Bis(2-ethylhexyl)phalate							5020	
Bromomethane	X		NP	X			2520	
Cadmium and compounds							7048	Solid, use Std. Hi-Vol
Carbon disulfide	X		NP	X			1600	
Carbon Tetrachloride	X	B	X	X			1003	
Chlordane	X			X	X			
Chloroaniline (p)	NP			NP				No validated Method
Chlorobenzene	X	X		X			1003	
Chloroform	X	B	X	X			1003	
Chloromethane (methyl chloride)	X	B	NP		NP			
Chlorophenol								Needs XAD-2 Backup
Chloroprene (Neoprene)	X	X	NP	X			1002	
Chromium and compounds							7024	Solid, use Std. Hi-Vol
Copper cyanide							7029	Solid, use Std. Hi-Vol.

TABLE 12-12 (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Cresol (o)							2001	Syn: methylphenol
Cresol (p)							2001	Syn: methylphenol
Cyanide	X						7904	
Dichloro-2-butene (1,4)	X	X		X				
Dichloro benzene (1,2)	X	X		X			1003	
Dichloro benzene (1,4)	X	X		X			1003	
Dichlorodifluoromethane	X	NP	NP					NIOSH 1012 should work
Dichloroethane (1,1) [ethylidine chloride]	X	X	NP	X			1003	
Dichlorophenoxyacetic acid (2,4)	X				NP		5001	Syn: 2,4-D
Dichloropropane (1,2)	X	X		X			1013	Method 1003 may be used
Dichloropropene (1,3)	X	NP		X				
Diethyl phthalate								No method identified
Dinotrotoluene (2,4)								Yellow crystals, use Hi-Vol
Dioxane (1,4)	X	X		X			1602	
Diphenylhydrazine (1,2)								No method identified
Ethylene dibromide	X	B		X			1008	Syn: 1,2-dibromoethane
Ethylene dichloride	X	B		X			1003	Syn: 1,2-dichloroethane
Fluorides							7902	Std. Hi-Vol for particulate fraction
Heptachlor								Waxy solid, use Std. Hi-Vol
Hexachlorobutadiene	X							

1 Blank spaces indicate that the method is inappropriate for that compound
2 B = small breakthrough volume for adsorbent
3 NP = t proven for this adsorbent, but may work
4 X = eptable media for collection

TABLE 12-12. (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Hexachloroethane		NP		X			1003	Syn: perchloroethane
Isobutanol		NP		X			1401	Syn: isobutyl alcohol
Lead and compounds							7802	Mostly particulate, use Hi-Vol
Mercury and compounds							7300	Mostly particulate, use Hi-Vol
Methacrylonitrile	X		NP	X				
Methyl ethyl ketone	X	X					2500	Syn: 2-butanone
Methyl methacrylate	X	NP		X				
Methylene chloride		B	X	X			1005	Syn: dichloromethane
Naphthalene	X				X		5515	Method TO-4 needs XAD-2
Nickel and compounds							7300	Mostly particulate, use Hi-Vol
Nitrobenzene	X	X		X			2005	
Nitrophenol	X	NP		X				
Parathion					NP		5012	
Pentachlorobenzene	X	NP		X				
Pentachloroethane	X	X		X				
Pentachlorophenol	X	NP						
Perchloroethylene	X	X		X				Syn. Tetrachloroethylene
Phenol	X	X		X			3502	
Phorate	X			X				
Pyridine	X							
Resorcinol	X							
Styrene	X	NP		X			1501	Syn. Polystyrene

TABLE 12-12. (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
TCDD (2,3,7,8)					X			
Toluene	X	X	X	X			1501	
Toxaphene	X				NP			Syn: Chlorinated camphene
Trichlorobenzene	X	NP		NP				
Trichloroethane (1,1,1)	X	B	X	X			1003	Syn: Methyl Chloroform
Trichloroethylene	X	X	X	X				
Trichloropropane (1,2,3)	X	X		X				
Vanadium pentoxide								Mostly particulate, use Hi-Vol
Vinyl acetate	X			X				
Vinyl chloride	X		X	X			1007	Syn: 1,1-dichloroethene
Vinylidene chloride (1,1 dichloroethylene)	X		X	X				
Xylene (m, o, p)	X	X		X			1501	Syn: dimethylbenzene
Zinc oxide							7530 and 7502	Solid, use Std. Hi-Vol

Table 12-13

Compounds Successfully Monitored Using EMSL-RTP Tenax Sampling Protocols

2-Chloropropane
1,1-Dichloroethene
Bromoethane
1-Chloropropane
Bromochloromethane
Chloroform
Tetrahydrofuran
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon tetrachloride
Dibromomethane
1,2-Dichloropropane
Trichloroethene
1,1,2-Trichloroethane
2,3-Dichlorobutane
Bromotrichloromethane
Toluene
1,3-Dichloropropane
1,2-Dibromomethane
Tetrachloroethene
Chlorobenzene
1,2-Dibromopropane
Nitrobenzene
Acetophenone
Benzonitrite
Isopropylbenzene
p-Isopropyltoluene
1-Bromo-3-chloropropane
Ethylbenzene
Bromoform
Ethenylbenzene
o-Xylene
1,1,2,2-Tetrachloroethane
Bromobenzene
Benzaldehyde
Pentachloroethane
4-Chlorostyrene
3-Chloro-1-propene
1,4-Dichlorobutane
1,2,3-Trichloropropane
1,1-Dichloroethane
2-Chlorobutane
2-Chloroethyl vinly ether
1,1,1,2-Tetrachloroethane
p-Dioxane
Epichlorohydrin
1,3-Dichlorobutane
p-Dichlorobenzene
cis-1,4-Dichloro-2-butene
n-Butyl benzene
3,4-Dichloro-1-butene
1,3,5-Trimethyl benzene

Thermal desorption is accomplished by rapidly heating the sorbent tube while a stream of inert gas flushes desorbed organics directly onto the GC column. Generally a secondary trap (either another sorbent or a cryogenically cooled loop) is used to hold the organics until injection into the GC column, but this step precludes multiple analyses of the sample.

Chemical desorption involves flushing the sorbent tube with an organic solvent, and analysis of the desorbed organics by GC or GC/MS. Since only a portion of the solvent is injected into the GC, sensitivity is lower than with thermal adsorption. However, reanalysis of samples is possible. The most common application of chemical desorption is for analysis of workplace air samplers, where relatively high concentrations of organics are expected.

The primary advantages of sorbent techniques are their ease of use and ability to sample large volumes of air. Sorbent cartridges are commercially available for many applications, and can easily be adapted to portable monitoring pumps or personal samplers. A wide variety of sorbent materials are available, and sorbent traps can be used singly or in series for maximum retention of airborne pollutants. Sorbent methods are especially applicable to integrated or long-term sampling, because large volumes of air can be passed through the sampling tube before breakthrough occurs.

In choosing a sorbent method, the advantages and limitations of specific methods should be considered along with general limitations of sorbents. Some important considerations are discussed below.

- Sorbents can be easily contaminated during manufacturing, shipping or storage. Extensive preparation (cleaning) procedures are generally needed to insure that the sorbent is free from interfering compounds prior to sampling. Tenax, for example, is often contaminated with benzene and toluene from the manufacturing process, requiring extensive solvent extraction and thermal conditioning before it is used. Once prepared, sampling cartridges must be protected from contamination before and after sampling.

- No single adsorbent exists that will retain all vapor phase organics. The efficiency of retention of a compound on a sorbent depends on the chemical properties of both compound and sorbent. Generally, a sorbent that works well for nonpolar organics such as benzene will perform poorly with polar organics such as methanol, and vice versa. Highly volatile compounds such as vinyl chloride will not be retained on weakly adsorbing materials such as Tenax, while less volatile compounds will be irreversibly retained on strong adsorbents such as charcoal. The optimal approach involves use of a sorbent that will retain a wide range of compounds with good efficiency, supplemented by techniques specifically directed towards "problem" compounds.

- Tenax-GC is a synthetic polymeric resin which is highly effective for volatile nonpolar organics such as aliphatic and aromatic hydrocarbons, and chlorinated organic solvents. Table 12-13 lists compounds that have been successfully monitored using a Tenax sorption protocol. Tenax has the important advantage that it does not retain water. Large amounts of water vapor condensing on a sorbent reduces collection efficiency and interferes with GC and GC/MS analysis. Another advantage of this material is the ease of thermal or chemical desorption.

  The major limitation of Tenax is that certain highly volatile or polar compounds are poorly retained (e.g., vinyl chloride, methanol). Formation of artifacts (i.e., degradation products from the air contaminant sample collected due to hydrolysis, oxidation, photolysis or other processes) on Tenax has also been noted, especially the oxidation of amines to form nitrosamines, yielding false positive results for the latter compounds.

  Carbon sorbents include activated carbon, carbon molecular sieves, and carbonaceous polymeric resins. The major advantage of these materials is their strong affinity for volatile organics, making them useful for highly volatile compounds such as vinyl chloride. The strength of their sorptive properties is also the major disadvantage of carbon sorbents because some organic compounds may become irreversibly adsorbed on the carbon. Thermal desorption of compounds with boiling points above approximately 80°C is not feasible due to the high temperature (400°C) required. Carbon adsorbents will retain some water, and therefore may not be useful in high humidity conditions.

In addition to the Tenax and carbon tube sampling methods shown above, passive sorption devices for ambient monitoring can be used. These passive samplers consist of a portion of Tenax or carbon held within a stainless steel mesh holder. Organics diffuse into the sampler and are retained on the sorbent material. The sampling device is designed to fit within a specially constructed oven for thermal desorption. Results from these passive samplers were reported to compare favorably with pump-based sorbent techniques. Because of the difficulty of determining the volume of air sampled via passive sampling, these devices would appear to be mainly applicable for screening purposes.

- Polyurethane foam (PUF) has been used extensively and effectively for collection of semivolatile organics from ambient air. Semivolatiles include PCBs and pesticides. Such compounds are often of concern even at very low concentrations. A significant advantage of PUF is its ability to perform at high flow rates, typically in excess of 500 liters per minute (l/m). This minimizes sampling times.

PUF has been shown to be effective for collection of a wide range of semivolatile compounds. Tables 12-14 and 12-15 list compounds that have been successfully quantified in ambient air with PUF. Compounds that have shown poor retention or storage behavior with PUF include hexachlorocyclohexane, dimethyl and diethylphthalates, mono- and dichlorophenols, and trichloro- and tetrachlorobenzenes. These compounds have higher vapor pressures, and may be collected more effectively with Tenax or with resin sorbents such as XAD-2.

PUF is easy to handle, pre-treat, and extract. Blanks with very low contamination concentations can be obtained, as long as precautions are taken against contamination after pretreatment. Samples have been shown to remain stable on PUF during holding times of up to 30 days. PUF

TABLE 12-14. SUMMARY LISTING OF ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER AND SUBSEQUENT ANALYSIS WITH AN ELECTRON CAPTURE DETECTOR (GC/ECD)[a]

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Polychlorinated Biphenyls (PCBs)

Aroclor 1221[c]
Aroclor 1232[d]
Aroclor 1242[a]
Aroclor 1016[c]
Aroclor 1248[d]
Aroclor 1254[a]
Aroclor 1260[a]

Chlorinated Pesticides

α-chlordane[a]
Y-chlordane[a]
Chlordane (technical)[a]
Mirex[a]
α -BHC[a]
β-BHC[d]
-BHC (Lindane)[a]
-BHC[d]
p,p'-DDD[d]
p,p'-DDE[a]
p, p'-DDT[a]
Endosulfan I[a]
Heptachlor[d]
Aldrin[a]

Polychlorinated Napthalenes (PCNs)

Halowax 1001[c]
Halowax 1013[c]

Chlorinated Benzene

1,2,3-Trichlorobenzene[a]
1,2,4-Trichlorobenzene[d]
1,3,5-Trichlorobenzene[d]
1,2,3,4-Tetrachlorobenzene[a]
1,2,3,5-Tetrachlorobenzene[d]
1,2,4,5-Tetrachlorobenzene[d]
Pentachlorobenzene[a]
Hexachlorobenzene[a]
Pentachloronitrobenzene[a]

Chlorinated Phenols

2,3-Dichlorophenol[b]
2,4-Dichlorophenol[b]
2,5-Dichlorophenol[b]
2,6-Dichlorophenol[b]
3,4-Dichlorophenol[b]
3,5-Dichlorophenol[b]
2,3,4-Trichlorophenol[d]
2,3,5-Trichlorophenol[d]
2,3,6-Trichlorophenol[d]
2,4,5-Trichlorophenol[a]
2,4,6-Trichlorophenol[d]
3,4,5-Trichlorophenol[d]
2,3,4,5-Tetrachlorophenol[d]
2,3,4,6-Tetrachlorophenol[d]
2,3,5,6-Tetrachlorophenol[d]
Pentachlorophenol[a]

[a] Method validation data for all components, unless otherwise noted, are available in the literature. This includes collection efficiency data and/or retention efficiency data, method recovery data, and in some cases, storage stability data on selected isomers from this compound class.

[b] Method validation data not presently available in the literature for either a low or high volume sampling procedure. Dichlorophenols, however, are amenable to the same analytical protocols suggested for the higher molecular weight clorophenol isomers (trichloro, tetrachloro, and pentachloro). Users are cautioned that sample collection efficiencies may not be as high for dichlorophenols as for the higher molecular weight chlorophenols. Collection/retention efficiency data should be generated for each specific program.

[c] Validation data employing low volume sampling conditions not presently available in literature. Component has, however, been evaluated using high volume PUF sampler.

[d] Actual validation data for isomer(s) employing low volume PUF sampler not available in literature. Behavior under low volume sampler conditions should be similar to other structural isomers listed. Component is amenable to analytical scheme employing GC/ECD

TABLE 12-15. SUMMARY LISTING OF ADDITIONAL ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER

Polynuclear Aromatic Hydrocarbons[a]

Napthalene
Biphenyl
Fluorene
Dibenzothiophene
Phenanthrene
Anthracene
Carbazole
2-Methylanthracene
1-Methylphenanthrene
Fluoranthene
Pyrene
Benzo(a)fluorene
Benzo(b)fluorene
Benzo(a)anthracene
Chrysene/triphenylene
Benzo(b)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
o-Phenylenepyrene
Dibenzo(ac)/(ah)anthracene
Benzo(g,h,i)perylene
Coronene

Herbicide Esters

2,4-D Esters, isopropyl[c]
2,4-D Esters, butyl[c]
2,4-D Esters, isobutyl[c]
2,4-D Esters, isooctyl[c]

Organophosphorous Pesticides

Mevinphos[b]
Dichlorvos[c]
Ronnel[c]
Chlorpyripos[c]
Diazinon[c]
Methyl parathion[c]
Ethyl parathion[c]

Carbamate Pesticides

Propoxur[c]
Carbofuran[c]
Bendiocarb[c]
Mexacarbate[c]
Carbaryl[c]

Urea Pesticides

Monuron[c]
Diuron[c]
Linuron[c]
Terbuthiuron[c]
Fluometuron[c]
Chlorotoluron[c]

Triazine Pesticides

Simazine[c]
Atrazine[c]
Propazine[c]

Pyrethrin Pesticides

Pyrethrin I[c]
Pyrethrin II[c]
Allethrin[c]
d-trans-Allethrin[c]
Dicrotophos[c]
Resmethrin[c]
Fenvalerate[c]

[a] These components have been reported in the literature using polyurethane foam samplers. Users are cautioned that this listing is provided solely as a working reference. Method validation studies including collection efficiencies, retention efficiencies, etc. employing the sampling procedures cited in this document have not been conducted. Procedures other than those noted in this document may be more applicable in routine use.

[b] Validation data employing low volume sampling conditions not presently available in literature. Component, however, has been evaluated using high volume PUF sampler.

[c] Sampler evaluation data for these compound classes using a low volume (PUF) sampler contained in the literature.

concentration methods have shown excellent collection efficiency and recovery of sorbed compounds from the material.

Most PUF methods specify the use of a filter ahead of the PUF cartridge, to retain particulates. The filter prevents plugging of the PUF which would reduce air flow through the sorbent. Some methods recommend extracting the filter separately to obtain a value for particulate organics. However, because most semivolatile compounds have sufficient vapor pressure to volatilize from the filter during the collection period, particulate measurements may not be representative of true particulate concentrations. Therefore, results from the PUF analyses may overestimate gaseous concentrations of semi-volatile compounds due to volatilization of semi-volatiles originally collected on the sampler inlet filter and subsequently collected by the PUF cartridge.

- Cryogenic methods for capturing and collecting volatile organics involve pulling air through a stainless steel or nickle U-tube immersed in liquid oxygen or liquid argon. After sampling, the tube is sealed, stored in a coolant, and returned to the laboratory for anlaysis. The trap is connected to a GC, rapidly heated, and flushed into a GC or GC/MS for analysis.

The major advantage of cryogenic concentration is that all vapor phase organics, except the most volatile, are concentrated. This is a distinct advantage over sorbent concentration, which is especially selective for particular chemical classes. Contamination problems are minimal with cryogenic methods because a collection media is not required.

Several disadvantages limit the current usefulness of cryogenic methods, including:

- Samplers rapidly become plugged with ice in high humidity conditions. This limits the volume of air that can be sampled.
- The entire sample is analyzed at once, enhancing sensitivity but making multiple analyses of a sample impossible.

- The necessity of handling and transporting cryogenic liquids makes this method cumbersome for many sampling applications.

- There is a possibility of chemical reactions between compounds in the cryogenic trap.

Whole air sampling--Air may be collected without preconcentration for later use in direct GC analysis or for other treatment. Samples may be collected in glass or stainless steel containers, or in inert flexible containers such as Tedlar bags. Rigid containers are generally used for collection of grab samples, while flexible containers or rigid containers may be used to obtain integrated samples. Using a flexible container to collect whole air samples requires the use of a sampling pump with flow rate controls. Sampling with rigid containers is performed either by evacuating the container and allowing ambient air to enter, or by having both inlet and outlet valves remain open while pumping air through the container until equilibrium is achieved.

Whole air sampling is generally simple and efficient. Multiple analyses are possible on samples, allowing for good quality control. This method also has the ability to be used for widely differing analyses on a single sample. The method has been widely used, and a substantial data base has been developed.

Problems may occur using this method due to decomposition of compounds during storage and loss of some organics by adsorption to the container walls. Sample stability is generally much greater in stainless steel containers than in glass or plastic. Whole-air sampling is limited to relatively small volumes of air (generally up to 20 liters due to the impracticality of handling larger sample collection containers), and has higher detection limits than some sorbent techniques.

Impinger collection--Impinger collection involves passing the air stream through an organic solvent. Organics in the air are dissolved in the solvent, which can then be analyzed by GC/MS. Large volumes of air sampled cause the collection solvent to evaporate. In addition, collection efficiency is dependent on flow rate of the gas, and on the gas-liquid partition coefficients of the individual compounds. However, there are certain specialized applications of impinger sampling that have been found to be preferable to alternate collection techniques (e.g., sampling for aldehydes and ketones).

Certain compounds of interest are highly unstable or reactive, and will decompose during collection or storage. To concentrate and analyze these compounds, they must be chemically altered (derivatized) to more stable forms. Another common reason for derivatization is to improve the chromatographic behavior of certain classes of compounds (e.g., phenols). Addition of the derivatization reagent to impinger solvent is a convenient way to accomplish the necessary reaction.

A widely used method for analysis of aldehydes and ketones is a DNPH (dinitrophenylhydrazine) impinger technique. Easily oxidized aldehydes and ketones react with DNPH to form more stable hydrazone derivatives, which are analyzed by high performance liquid chromatography (HPLC) with a UV detector. This method is applicable to formaldehyde as well as less volatile aldehydes and ketones.

Direct analysis--A method not requiring preconcentration or separation of air components is highly desirable, because it avoids component degradation or loss during storage. Air is drawn through an inert tube or probe directly into the instrument detector. Several portable instruments exist that can provide direct air analysis, including infrared spectrophotometers, mobile MS instruments, and portable FID detectors. Some of these instruments have been discussed in the section on screening methods.

Mobile mass spectrometry has been used to compare upwind and downwind concentrations of organic pollutants at hazardous waste management facilities. The advantage of the multiple mass spectrometer configuration (MS/MS or triple MS) over a single MS system is that multiple systems can identify compounds in complex mixtures without pre-separation by gas chromatography. Major limitations of MS/MS methods are low sensitivity and high instrument cost.

In summary, of the methods described in this subsection, the majority of vapor-phase organics can be monitored by use of the following sampling methods:

- Concentration on Tenax or carbon adsorbents, followed by chemical or thermal desorption onto GC or GC/MS.
- Sorption on polyurethane foam (PUF) cartridges, followed by solvent extraction.
- Cryogenic trapping in the field.
- Whole-air sampling.

12.6.2.2.1.2 Particulate Organics

Certain hazardous organic compounds of concern in ambient air are primarily associated with airborne particles, rather than in the vapor phase. Such compounds include dioxins, organochlorine pesticides, and polyaromatic hydrocarbons. Therefore, to measure these compounds accurately, it is necessary to monitor particulate emissions from units of concern.

Measurements of particulate organics is complicated because even relatively nonvolatile organics exhibit some vapor pressure, and will volatilize to a certain extent during sampling. The partitioning of a compound between solid and gaseous phases is highly dependent on the sampling conditions (e.g., sampling flow rate, temperature). Particulate sampling methods generally include a gas phase collection device after the particulate collector to trap those organics that become desorbed during sampling.

The most common methods used for collection of particles from ambient air are:

- Filtration
    - Cellulose Fiber
    - Glass or Quartz Fiber
    - Teflon Coated Glass Fiber

  - Membranes

- Centrifugal Collection (e.g., cyclones)
- Impaction
- Electrostatic Precipitation

The standard sampling method for particulates, is filtration. Teflon-coated glass membranes generally give the best retention without problems with separating the particulates sampled from the filter. Problems, however, may be caused by desorption of organics from the filter, by chemical transformation of organics collected on the filter, and with chemical transformation of organics due to reaction with atmospheric gases such as oxides of nitrogen and ozone. These problems are worsened by the large volumes of air that must be sampled to obtain sufficient particulate material to meet analytical requirements. For example, to obtain 50 milligrams of particulates from a typical air sample, 1000 cubic meters of air must be sampled, involving about 20 hours of sampling time with a high-volume sampling pump.

Despite the drawbacks mentioned above, filtration is currently the simplest and most thoroughly tested method of collecting particulates for organic analysis. Other methods, such as electrostatic precipitation, make use of electrical charge or mechanical acceleration of the particles. The effect of these procedures on compound stability is poorly understood.

12.6.2.2.2 Monitoring Inorganic Compounds in Ambient Air

12.6.2.2.2.1 Particulate Metals

Metals in ambient air can occur as particulates or can be adsorbed on other particulate material. Metals associated with particulate releases are effectively collected by use of filter media allowing for the collection of adequate samples for analysis of a number of particulate contaminants.

Collection on filter media--Sampling methods for particulate metals are generally based on capture of the particulate on filter media. For the most part, glass fiber filters are used; however, organic and membrane filters such as cellulose ester and Teflon can also be used. These membrane filters demonstrate greater uniformity of pore size and, in many cases, lower contamination levels of trace metals than are found in glass fiber filters. Analytical procedures described in the following reference can be utilized to analyze particulate samples.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA SW-846. GPO No. 955-001-00000-1. Office of Solid Waste, Washington, D.C. 20460.

Hi-Vol collection devices--The basic ambient air sampler is the high volume sampler which can collect a 2000 cubic meter sample over a 24-hour period and capture particulates on an 8 x 10 inch filter (glass fiber) as described in 40 CFR Part 50. It has a nominal cut point of 100um for the maximum diameter particle size captured. A recent modification involves the addition of a cyclone ahead of the filter to separate respirable and non-respirable particulate matter. Health criteria for particulate air contaminants are based on respirable particulate matter.

Personnel samplers--Another particulate sampling method involves the use of personnel samplers according to NIOSH methods (NIOSH, 1984). The NIOSH methods are intended to measure worker exposure to particulate metals for comparison to OSHA standards. A 500-liter air volume is sampled at approximately 2 liters per minute. This method is most efficient when less than 2 mg total particulate weight are captured. Capture of more than 22 mg may lead to sample losses during handling of the sample. The preferred filter medium is cellulose ester (47 mm diameter) which will dissolve during the standard acid digestion.

The NIOSH method, however, is not recommended for the RFI for several reasons. The NIOSH analytical methods (and good QA/QC practices) require several aliquots of the sample to be prepared for best analytical results. The 47 mm filter is too small for aliquoting; therefore, use of the NIOSH method would require the simultaneous operation of several sampling systems. More importantly, the 500 liter sample volume generaly does not provide sufficient particulate matter for the analytical methods to detect trace ambient levels of metals. The method is best suited for industrial hygiene applications.

Dichotomous Samplers--Dichotomous samplers (virtual impactors) have been developed for particle sizing with various limit cutpoints for use in EPA ambient monitoring programs. These samplers collect two particulate fractions on separate 37 mm diameter filters from a total air volume of about 20 cubic meters. The standard sampling period is 24 hours. Teflon filters are generally recommended by sampler manufacturers because they exhibit negligible particle penetration and result in a low pressure drop during the sampling period. However, glass fiber and cellulose filters are also acceptable.

The need for multiple extractions would require multiple sampling trains. If the two filters are combined to form one aliquot and extracted together, they will provide sufficient sensitivity for some but not all analytical procedures and defeat the purpose of fractioning the sample. The use of the dichotomous sampler is, therefore, limited.

12.6.2.2.2.2 Vapor Phase Metals

Most metallic elements and compounds have very low volatilites at ambient temperatures. Those that are relatively volatile, however, require a different sampling method than used for collection of particulate forms, although analytical techniques may be similar. For the purpose of ambient monitoring, vapor-phase metals are defined as all elements or compounds that are not effectively captured by standard filter sampling procedures. Available methods for the measurement of vapor phase metals are presented in Tables 12-16 and 12-17. These available methods are generally developed for industrial hygiene applications by NIOSH.

The methods for measuring vapor-phase metals presented in Tables 12-16 and 12-17 have undergone limited testing for precision and accuracy and have had matrix interferences documented. Therefore, they should be used in lieu of any methods which have no supporting data.

Several methods are suitable for quantification of vapor-phase mercury. If elemental mercury is to be measured, the silver amalgamation technique with

TABLE 12-16. SAMPLING AND ANALYSIS METHODS FOR VOLATILE MERCURY

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
*NIOSH P&CAM 6000	Particulate, organic and elemental mercury	Sampling train consists of membrane filter to capture particulate Hg, followed by Carbosieve B to trap organic Hg, and then silver coated Chromosorb P (CP) to collect elemental Hg. Each section is analyzed separately by thermal desorption into a flameless AA. Filters are acid digested, reduced to Hg and amalgamated on Ag CP prior to the AA analysis step.	- Standard method - Permits measurement of all three types of mercury - Method selective to mercury	- Requires use of complex desorption unit - Cl_2 interferes with sampling - Separation of organic and metallic mercury is uncertain at 0.001 Hg/total Hg - Requires preparation of special sorbents
NIOSH SCP-S342	Organic mercury	Filter to separate particulate; adsorb organic Hg on Carbosieve B; thermally desorb into flameless AA unit	- Standard method - Option to P&CAM 175 if organic mercury is only concern - Range is 20-80 $\mu g/m^3$ with a 3 liter sample volume	- Requires complex thermal desorption unit
EPA Method 101	Particulate and vaporous mercury	Collection in acidified 0.1 NHCℓ impinger solution; analysis by NAA or optionally by cold vapor AA	- Standard method - Detection limit of 1 $\mu g/m^3$ - Fairly stable reagent - Same reagent has been used for volatile Pb (Ref. 572)	- NAA expensive ($125/sample) and not routinely available - Ice interferes with cold vapor AA method at low concentrations of Hg - Instability of collected Hg compounds in solution has been reported
Canadian EPS Standard Method	Particulate and vaporous mercury	Collection in impinger solution of 10% H_2SO_4/2% $KMnO_4$; analysis by cold vapor AA	- Standard method - Collection efficiency ≥ 90% - $KMnO_4$ and AA compatible - AA costs ≃ $30/sample - Reagent gives low blank levels	- $KMnO_4$ reagent must be prepared within 12 hours of use - Short sample holding time - Reagent can be easily expended in oxidizing and organic matrices

TABLE 12-16. (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
Environment Canada	Vaporous mercury or particulate mercury	Vaporous mercury is collected by amalgamation on silver. Particulate is collected on microquartz filters. Both are analyzed by thermal desorption and/or pyrolysis with re-amalgamation; then thermal desorption for determination by UV absorption at 253.7	- Standard method for ambient air - Used in range of 4-22 mg/m^3 - Claimed to be "inexpensive"	- Complex desorption/amalgamation unit
3M Badge	Elemental Hg vapor	Passive device-diffusion of Hg through membrane, amalgamation on gold, analysis of badges performed by 3M	- Very simple and mercury specific method - Requires no analysis to be performed by users - Gives 8-hour time weighted average and concentrations of up to 20 μg/m^3	- Cl_2 interferes with sampling efficiency - High H_2S and SO_2 also interfere - Temperature variations affect diffusion rates and must be corrected for
MSA Method	Elemental and organic mercury	Adsorb mercury on iodine impregnated charcoal; place in tantalum boat and volatilize	- Simple equipment requirements - Range of 50-200 μg/m^3 tested	- Large coefficient of variation - Quality of results are very much operator dependent - Only works well at 200 μg/m^3
Hopcalite Method	Elemental and organic mercury	Adsorb on hopcalite; dissolve sorbent and mercury in HNO_3 + HCl; analyze by cold vapor AA	- Simple equipment requirement - Evaluated in range of 50-200 μg/m^3	- Does not provide for analysis of particulate mercury - Insufficient performance data in available literature

TABLE 12-16 (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
*Silver amalgamation and APHA	Vaporous elemental mercury	Amalgamation on silver wool or silver gauge; thermal desorption with analysis by flameless AA or UV absorption	- Substantial information on the method; interferences provided in the references - Ag wool-24 hour sample can be used with 15 ng-10 pg/m^3 levels - Ag gauge ≤ 2 hour sample can give concentrations of 5 ng-100 μg/m^3	- Collection efficiency for organic mercury is in question - Oxidants could interfere with sampling procedure unless removed before reaching silver
Impinger/Dithizone	Organic, particulate and vaporous mercury	Collect in impinger solution of 0.1 NiCl and 0.5 m HCl; analyze by the dithizone colorimetric method	- Efficient capture of all three types of volatile mercury	- Dithizone method suffers from high blanks, interference from SO_2 and interference from several other metals - Mercury compounds collected in HCl are unstable
Jerome Instrument Corp., Model 411, Gold Film Hg Vapor Analyzer	Elemental mercury	Onsite monitor-amalgamation of Hg on gold, measure concentration by change in gold foil resistance	- Selective for mercury - Direct reading eliminates sample transport and analysis - Concentration range from μg/m^3 to mg/m^3	- Monitor costs $3500-$4000 - May suffer interference from oxidants as noted for 3M badges

* Recommended methods

TABLE 12-17. SAMPLING AND ANALYSIS OF VAPOR STATE TRACE METALS (EXCEPT MERCURY)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
Antimony	NIOSH S243	Stibine (SbH_3)	Adsorb on mercuric chloride impregnated silica gel; extract with concentration HCl; oxidize Sb(111) to Sb(V) with ceric sulfate; colorimetric analysis by Rhodamine	- Standard method	- Range only 0.1-1.0 ng/m^3 using a 20-liter sample - Analytical interferences by Pb(III), Tl(I), and Sb(II)
Arsenic	NIOSH P&CAM 6001	Arsine (AsH_3)	Adsorb on charcoal; desorb with HNO_3; analyze by furnace AA	- Standard method	- Possible breakthrough at high concentrations
	NIOSH S229 NIOSH 7900	Arsine (AsH_3)	Same as P&CAM 265 except that HNO_3 desorption is performed with 10 ml rather than 1 ml	- Standard method - Working range 0.09-0.1 mg/m^3	- Possible breakthrough at high concentrations - Earlier version of P&CAM 265
		As_2O_3 and others	Absorb in dilute NaOH solution; analytical procedure not specified but it may be suitable to use arsine generation or furnace AA	- Only method proposed for AS_2O_3 in available literature - Relatively simple	- No supporting data available
*Lead	NIOSH S383 and S384	Tetraethyl lead and tetramethyl lead	Adsorb on XAD-2; desorb with pentane; analysis by GC	- Standard method - Permits separation of the various alkyl lead compounds - Range 0.045-0.20 ng/m^3 (as Pb) - Can alter GC conditions to remove interferences with analysis	- Compound identification only by GC retention times; must verify
		Alkyl lead compounds	Collect in HCl/NiCl impinger solution; analyze by dithizone colorimetric method when 8-hour sampling period or by AA for 24 hour sample	- Near 100% collection efficiency - Dithizone detection limit - 10 µg/m^3 - AA detection limit - 0.2 - 10 µg/m^3	- Very little information in literature - Dithizone method may have same problems noted elsewhere for other elements

TABLE 12-17. (continued)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
		Alkyl lead compounds	Adsorb on activated carbon; digest with HNO_3 + $HClO_4$; analyze by dithizone method	- Good collection efficiency - Low detection limits possible	- No data available - Dithizone method may have interferences as noted above
Nickel	N1OSH P&CM 344	Nickel tetracarbonyl ($Ni(CO)_4$)	Adsorb on charcoal; desorb with dilute HNO_3; analyze by furnace AA	- Standard method - AA specific for Nickel - Range 2-60 μg/m³	- Sorbeat capacity limits upper concentration
	Ref. 120, 142	Nickel tetracarbonyl ($Ni(CO)_4$)	Absorb in 3% HCl impinger solution; analyze by colorimetric method in which color development in chloroform phase is measured	- Detection limit - 0.001 ppm	- Not a standard method - Interference may occur from other Nickel compounds, Cu, Pb, Cr, Se and V
Selenium		SeO_2, H_2SeO_3	Collect in impinger with aqueous solution of Na_2SO_3, Na_2S, or NaOH, analyze by NAA, AA, GC, colorimetry, fluorimetry, ring oven techniques, or catalytic methods	- Only method suggested in literature for volatile Se	- No data to support this method

thermal desorption and flameless AA (atomic absorption) analysis is recommended. This technique is presented in American Public Health Association (APHA) Method 317, which can achieve nanogram per cubic meter detection limits. If organic and/or particulate mercury are also to be determined, NIOSH methods (NIOSH, 1984) are recommended. These methods can measure all three airborne mercury species, but require a complex two stage thermal desorption apparatus.

12.6.2.2.2.3 Monitoring Acids and Other Compounds in Ambient Air

Monitoring for acids and other inorganic/non-metal compounds (e.g., hydrogen sulfide) in the ambient air will generally require application of industrial hygiene technologies. Applicable methods have been compiled in the following references:

NIOSH. February 1984. NIOSH Manual of Analytical Methods. NTIS PB 85-179108. National Institute for Occupational Safety and Health. Cincinnati, OH.

ASTM. 1981. Toxic Materials in the Atmosphere. ASTM, STP 786. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association.

ACGIH. 1983. Air Sampling Instruments for Evaluation of Atmospheric Contamination. American Conference of Governmental Industrial Hygienists. Cincinnati, OH.

12.6.3 Stack/Vent Emission Sampling

EPA methods for source-sampling and analysis are documented in the following reference:

Code of Federal Regulations. 40 CFR Part 60, Appendix A: Reference Methods. Office of the Federal Register, Washington, D.C. 20460.

Additional guidance is available in the following references:

U.S. EPA. 1978. Stack Sampling Technical Information, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042 a, b, c. NTIS PB 80-161672, 80-1616680, 80-161698. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. February 1985. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. March 1984. Protocol for the Collection and Analysis of Volatile POHC's Using VOST. EPA-600/8-84-007. NTIS PB 84-177799. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. February 1984. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA-600/8-84-NTIS PB 84-145580. Washington, D.C. 20460.

U.S. EPA. November 1985. Practical Guide - Trial Burns for Hazardous Waste Incinerators. NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.

U.S. EPA. 1981. Source Sampling and Analysis of Gaseous Pollutants. EPA- APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1979. Source Sampling for Particulate Pollutants. EPA-APTI Course Manual 450. PB 80-188840, 80-174360, 80-182439. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste, Washington, D.C. 20460.

12.6.3.1. Vapor-Phase and Particulate Associated Organics

Generally, point source vapor-phase samples are obtained from the process vents and effluent streams either by a grab sample technique or by an integrated sampling train. Careful planning is necessary to insure that sampling and analytical techniqes provide accurate quantitative and qualitative data for measurements of vapor-phase organics. Considerations such as need for real-time (continuous) versus instantaneous or short-term data, compatibility with other compounds/parameters to be measured, and the need for onsite versus offsite analysis may all be important in the selection process.

Monitoring for complex organic compounds generally requires detailed methods and procedures for the collection, recovery, identification, and quantification of these compounds. The selection of appropriate sampling and analytical methods depends on a number of important considerations, including source type and the compounds/parameters of interest. Table 12-18 lists several sampling methods for various applications and compound classes (applicable to combustion sources). The first three methods listed are fixed-volume, grab-sampling methods. Grab sampling is generally the simplest technique to obtain organic emission samples.

Sample collection by the bag and canister sampling methods can be used to collect time-integrated samples. These methods also allow for a choice of sample volumes due to a range of available bag sizes (6, 12, and 20 liter capacities are typical). Bags of various materials are available, including relatively inert and noncontaminating materials such as Teflon, Tedlar, and Mylar. All sample collection bags types may have some sample loss due to adsorption of the contaminants collected to container walls. The bag sample is collected by inserting the bag into an airtight, rigid container (lung) and evacuating the container. The sample is drawn into the bag because reduced pressure in the container provides adequate suction to fill the bag. This procedure is presented in detail in 40 CFR, Part 60 Appendix A (Method 3).

TABLE 12-18. SAMPLING METHODS FOR TOXIC AND HAZARDOUS ORGANIC MATERIALS FROM POINT SOURCES

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Syringe Flow-through bottle Evacuated canister Tedlar bag (EPA Method 3)	Instantaneous grab Instantaneous grab Integrated grab Integrated grab	Non-combustion (storage tanks spray booths paint bake ovens, etc.) Low moisture content combustion emissions (boilers dry control incinerators, etc.).	Volatiles, C_1-C_{10} Volatiles, C_1-C_{10} Volatiles, C_1-C_{10} Volatiles, C_1-C_{10}	GC-FID[a] GC-MS[b] or GC-PID[c]	Sample size and therefore detectable concentration are limited by container size; ≥ 1 ppm. Bag samples are subject to absorptive losses of sample components.
EPA method 25	Two stage integrated grab train consisting of cold trap followed by evacuated S.S. tank.	Non-combustion and low moisture content combustion emissions as above.	Volatiles and semi-volatiles, C_1-C_{16}	Oxidation/ reduction followed by GC/FID.	Sample size is limited by tank volume. CO_2 and H_2O can produce significant interferences. System is complex/cumbersome.
-VOST[d]	Water-cooled sample gas, including condensate, is passed through dual in-series sorbent traps. Tenax GC in first tube followed by Tenax GC backed-up by charcoal in second tube.	Combustion emissions (boilers, hazardous waste incinerators, etc.).	Volatiles and semi volatiles, C_1-C_{16}, C_1-C_{10}	GC-MS GC-ECD GC-PID	Sample size is limited to 20 liters per pair of sorbent tubes. Sorbent tubes are susceptable to contamination from organics in ambient air during installation and removal from train.

TABLE 12-1b ,continued)

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Modified Method 5	Water-colled sample gas, with condensate is passed through single sorbent trap. Sorbent type dependent on compound(s) of interest.[e]	Combustion emission as for VOST.	Semi-volatiles, PCB's, other halogenated organics, C_7-C_{16}. $C1_{-1}$-$C1_{10}$	GC-ECD, GC-HECD, GC-MS	Single trap system does not provide check for breakthrough. Flow rate limited to approximately 1 cpm.
High Volume Modified Method 5	Sample gas is passed through condensers where moisture is removed before passing through two sorbent traps, primary followed by back-up. Flow rates of up to 5 cpm are achievable. Sorbent type dependent on compounds of interest.[e]	Combustion emissions.	Semi-volatiles, PCBs, other halogenated organics, C_7-C_{16}. C_1-C_{10}	GC-ECD, GC-HECD, GC-MS	High flow rate results in high sampling train pressure drop requiring large pump capacity.
SASS Train	Sample gas passes through a cold trap followed by an XAD-2 sorbent trap. Train is all stainless steel construction.	Combustion emissions (boilers, hazardous waste incinerators).	Semi-volatiles, and other, non-halogenated organics, C_7-C_{-16}	GC-ECD, GC-HECD, GC-MS	System is complex, large and cumbersome. Recovery of organics from cold trap can be difficult. S.S. construction makes train components highly susceptable to corrosion from acid gases especially HCl.

[a] GC-FID - gas chromatography with flame ionization detector.
[b] GC-MS - gas chromatography-mass spectrometry.
[c] GC-PID - gas chromatography-photoionization detector.
[d] VOST - volatile organic sampling train.
[e] Sorbents include Florisil, XAD-2 resin, and Tenax-GC among the most commonly used.

Source: Hazardous Waste Management, Vol. 35, No. 1, January 1985

Evacuated canisters are conventionally constructed of high grade polished stainless steel. There are many versions available ranging from units with torque limiting needle valves, purge free assemblies, internal electropolished surfaces and versions utilizing stainless steel beakers with custom designed tops and fittings. Also, different container materials may react differently with the sample. Therefore, sample storage time or sample recovery studies to determine or verify inertness of the sampling canister should be considered.

Canisters are generally used to collect samples by slowly opening the sample valve, allowing the vacuum to draw in the sample gas. In less than a minute, the container should equilibrate with the ambient atmospheric pressure. At that time, the sample valve is closed to retain the sample. To collect composite samples over longer intervals, small calibrated orifices can be inserted before the inlet valve to extend the time required for equilibration of pressures once the sample valve is opened.

The sample collection procedure for EPA Method 25 (U.S. EPA, 1981) is similar in principle to that for the evacuated canister. The train consists of a polished stainless steel canister with a cold condensate trap in series and prior to the canister to collect a higher boiling point organic fraction. This two fraction apparatus provides for separate collection of two concentration ranges of volatile organic compounds based on boiling point.

The following four sampling methods utilize sample concentration techniques using one or more sorbent traps. The advantages of these methods is an enhanced limit of detection for many toxic and hazardous organic compounds. These techniques are preferred due to their lower detection limit. The Modified Method 5 (MM5) sampling train (U.S. EPA, 1981) is used to sample gaseous effluents for vapor-phase organic compounds that exhibit vapor pressures of less than 2 mm Hg (at 20°C). This system is a modification of the conventional EPA Method 5 particulate sampling train. The modified system consists of a probe, a high efficiency glass or quartz fiber filter, a sorbent module, impingers, and related control hardware. The sample gas is passed through a single sorbent trap, containing XAD-2. The MM5 train is limited due to the single sorbent trap design that does not provide a backup for breakthrough. This is especially important when large volumes of sample are collected.

To minimize the potential for breakthrough, the MM5 train can be modified to provide a backup trap. However, this dual trap modification increases the pressure drop across the train, reducing the range of flow rates possible for sample collection. To overcome this pressure drop and maintain the desired flow rate, the high-volume MM5 train utilizes a much larger capacity pump.

The Source Assessment Sampling System (SASS) train is another comprehensive sampling train, consisting of a probe that connects to three cyclones and a filter in a heated oven module, a gas treatment section, and a series of impingers to provide large collection capacities for particulate matter, semivolatiles, and other lower volatility organics. The materials of construction are all stainless steel making the system very heavy and cumbersome. The stainless steel construction is also very susceptible to corrosion. This system can, however, be used to collect and concentrate large sample volumes providing for a much lower detection limit. Because of the sorbents used (generally XAD-2), its use is limited to the same class of lower volatility organics and metals as the MM5 train.

The Volatile Organic Sampling Train (VOST) has proven to be a reliable and accurate method for collection of the broad range of organic compounds. By using a dual sorbent and dual in-series trap design, the VOST train can supplement either the MM5 or SASS methods allowing for collection of more volatile species. However, VOST has several limitations, including a maximum sample flow rate of 1.0 liter/minute, and a total sample volume of 20 liters per trap pair. Therefore, frequent changes of the trap pairs are required for test periods that exceed 20 minutes. The frequent change of traps makes the samples more susceptible to contamination.

Any of the point source monitoring techniques described above can be adapted for use with the isolation flux chamber techniques described in Appendix D. For point sources where particulate emissions are of concern, the Modified Method 5 or SASS train (originally designed to measure particle emissions from combustion effluents) are also applicable and proven technologies.

Analytical methodologies for the techniques discussed above will vary with the technique used. While certain techniques will offer advantages over others in the measurement of specific contaminants, the investigator is advised to utilize standard methodologies whenever possible in performing the RFI. For example, use of the VOST and/or the MM5 train, and their associated analytical methodologies is recommended for point source monitoring of the applicable compounds. Descriptions for both of these methods are included in the 3rd Edition of "Test Methods for Evaluating Solid Waste" (EPA SW-846), 1986 (GPO No. 955-001-00000-1). Although these methods are designed for the evaluation of incinerator efficiencies, they are essentially point-source monitoring methods which can be adapted to most any point sources.

12.6.3.2 Metals

Although the emission of metallic contaminants is primarily associated with particulate emission from area sources caused by the transfer of material to and from different locations, wind erosion, or general maintenance and traffic activities at the unit, point source emission of particulate or vapor-phase metals can exist. Metallic constituents may exist in the atmosphere as solid particulate matter, as dissolved or suspended constituents of liquid droplets (mists), and as vapors.

Metals specified as hazardous constituents in 40 CFR Part 261, Appendix VIII are generally noted as the element and compounds "not otherwise specified (NOS)", as shown in Table 12-19, indicating that measurement of the total content of that element in the sample is required.

Vapor phase metals--For the purpose of point-source monitoring, vapor-phase metals will be defined as all elements or compounds thereof, that are not quantitatively captured by standard filter sampling procedures. These include volatile forms of metals such as elemental and alkyl mercury, arsine, antimony, alkyl lead compounds, and nickel carybonyl.

The sampling of point sources for vapor phase metals has not been a common or frequent activity for the investigation of air releases from solid waste management units. If a point source of vapor-phase metals is identified, the sampling approach

Table 12-19.

RCRA Appendix VIII Hazardous Metals and Metal Compounds

Antimony and compounds NOS[a]
Arsenic and compounds NOS[b]
Barium and compounds NOS[b]
Beryllium and compounds NOS
Cadmium and compounds NOS
Chromium and compounds NOS
Lead and compounds NOS
Mercury and compounds NOS[b]
Nickel and compounds NOS[b]
Selenium and compounds NOS[b]
Silver and compounds NOS[b]
Thallium and compounds NOS[b]

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[a] NOS = not otherwise specified.

[b] Additional specific compound(s) listed for this element.

identify the best available monitoring techniques, considering that many have been developed which are specific to single species rather than multiple species of many different metal elements. The primary references for identifying available techniques include National Institute of Occupational Safety and Health (NIOSH, 1984) methods, EPA methods such as those presented in SW-846 and in the Federal Register under the National Emissions Standards for Hazardous Air Pollutants (NESHAPs), and American Public Health Association (APHA, 1977) methods. The basic monitoring techniques include collection on sorbents and in impinger solutions. The particular sorbent or impinger solution utilized should be selected based on the specific metal species under investigation.

Particulate Metals Point-source releases to air could also require investigation of particulate metals. Source sampling particulate procedures such as the Modified Method 5 or SASS methods previously discussed are appropriate for this activity. EPA Modified Method 5 is the recommended approach. Modifications of this basic technique involving the collection of particulate material on a filter with subsequent analysis of the collected particulate for the metals of concern, could include higher or lower flow rates and the use of alternate filter media. Such modifications may be proposed when standard techniques prove to be inadequate. Several important particulate metal sampling methods are available in the NIOSH methods manuals (NIOSH, 1984); however, these methods were designed for ambient or indoor applications and may require modification if used on point sources.

12.7 Checklist

RFI Checklist - AIR

Site Name/Location ______________________________
Type of Unit ______________________________

1. Does waste characterization include the following information? (Y/N)

- Physical form of the waste ______
- Identification of waste components ______
- Concentrations of constituents of concern ______
- Chemical and physical properties of constituents of concern ______

2. Does unit characterization include the following information? (Y/N)

- Type of unit ______
- Types and efficiencies of control devices ______
- Operational schedules ______
- Operating logs ______
- Dimensions of the unit ______
- Quantities of waste managed ______
- Locations and spatial distribution/ variation of waste in the unit ______
- Past odor complaints from neighbors ______
- Existing air monitoring data ______
- Flow rates from vents ______

3. Does environmental setting characterization include the following information? (Y/N)

- Definition of regional climate ______
- Definition of site-specific meteorological conditions ______
- Definition of soil conditions ______

- Definition of site-specific terrain ________
- Identification of potential release receptors ________

4. Have the following data on the initial phase of the release characterization been collected? (Y/N)

    - Identification of "reasonable worst case" conditions ________
    - Meteorological conditions during monitoring ________
    - Release source conditions during monitoring ________
    - Basis for selection of monitoring constituents ________
    - Concentrations of released constituents at unit, facility and nearby actual offsite receptors based on monitoring or modeling and "reasonable worst case" conditions ________

5. Have the following data on the subsequent phase(s) of the release characterization been collected (Y/N)

    - Identification of "reasonable worst case" conditions ________
    - Meteorological conditions during monitoring ________
    - Release source conditions during monitoring ________
    - Basis for selection of monitoring constituents ________
    - Concentrations of released constituents at unit, facility and nearby actual offsite receptors based on monitoring or modeling and representative of reasonable "worst case" conditions ________

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SECTION 13

SURFACE WATER

13.1 Overview

The objective of an investigation of a release to surface water is to characterize the nature, extent, and rate of migration of the release to this medium. This section provides the following:

- An overall strategy for characterizing releases to the surface water system (e.g., water column, bottom sediments, and biota), which includes characterization of the source and the environmental setting of the release, and conducting a monitoring program that will characterize the release;
- A discussion of waste and unit source characteristics and operative release mechanisms;
- A strategy for the design and conduct of monitoring programs considering specific requirements of different wastes, release characteristics, and receiving water bodies;
- Recommendations for data organization and presentation;
- Appropriate field and other methods that may be used in the investigation; and
- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be facility and site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all instances; however, it identifies the information that is likely to be needed to perform release characterizations and identifies methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information collection for release characterization. This list is not a list of requirements for all releases to surface water. Some releases will involve the collection of only a subset of the items listed, while others will involve the collection of additional data.

Case Study Numbers 10, 11, 12 and 29 in Volume IV (Case Study Examples) illustrate various aspects of surface water investigations which are described below.

13.2 Approach for Characterizing Releases to Surface Water

13.2.1 General Approach

The general approach recommended for characterization of releases to surface waters consists of a series of steps summarized in Table 13-1. These steps outline a phased approach, beginning with evaluation of existing data and proceeding to design and implementation of a monitoring program, revised over time, as necessary, based on findings of the previous phase. Each of these steps is discussed briefly below.

The first step in the general approach is the collection and review of available information on the contaminant source and the environmental setting. Some information on the contaminant source will be available from several reports and other documents. The RCRA Permit, Compliance Order, or RFA report will provide a summary of information regarding actual or suspected releases from the various units. The facility owner or operator should be familiar with this information as a basis for further characterization of the release(s) in the RFI. In addition, thorough understanding of the environmental setting is essential to an adequate determination of the nature and extent of releases to surface waters. Monitoring data should also be reviewed focusing on the quality of the data. If the quality is determined to be acceptable, then the data may be used in the design of the monitoring program. Guidance on obtaining and evaluating the necessary

Table 13-1

Recommended Strategy for Characterizing Releases to Surface Water*

INITIAL PHASE

1. Collect and review preliminary information for use in formulating monitoring procedures.
   - Waste and unit characteristics
   - Surface water characteristics
   - Actual or suspected release characteristics
2. Identify additional information necessary to characterize release
   - Release location, frequency and form
   - Surface water characteristics (e.g., stream discharge, lake stratification)
   - Inter-media transport
   - Conceptual model of release
3. Develop monitoring procedures
   - Determine monitoring program objectives
   - Select monitoring constituents and indicator parameters
   - Select monitoring locations
   - Determine monitoring frequency
   - Incorporate hydrologic monitoring as necessary
   - Determine role of biomonitoring and sediment monitoring
4. Conduct initial monitoring phase
   - Collect samples under initial monitoring phase procedures and complete field analyses
   - Analyze samples for selected parameters and constituents
5. Collect, evaluate, and report results
   - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
   - Determine completeness and adequacy of collected data
   - Summarize and present data in appropriate format
   - Determine if monitoring program objectives were met
   - Determine if monitoring locations, constituents and frequency were adequate to characterize release (nature, extent, and rate)
   - Report results to regulatory agency

Table 13-1 (continued)

Recommended Strategy for Characterizing Releases to Surface Water*

SUBSEQUENT PHASES (If necessary)

1. Identify additional information necessary to characterize release
    - Identify additional information needs
    - Determine need to include or expand hydrologic, and sediment and bio-monitoring
    - Evaluate potential role of inter-media transport
2. Expand initial monitoring as necessary
    - Relocate, decrease, or increase number of monitoring locations
    - Add or delete constituents and parameters of concern
    - Increase or decrease monitoring frequency
    - Delete, expand, or include hydrologic, sediment or bio-monitoring
3. Conduct subsequent monitoring phases
    - Collect samples under revised monitoring procedures and complete field analyses
    - Analyze samples for selected parameters and constituents
4. Collect, evaluate and report results/identify additional information necessary to characterize release
    - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
    - Determine if monitoring program objectives were met
    - Determine if monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)
    - Identify additional information needs
    - Determine need to include or expand hydrologic, sediment, or bio-monitoring
    - Evaluate potential role of inter-media transport
    - Report results to regulatory agency

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* Surface water system is subject to inter-media transport. Monitoring program should incorporate the necessary procedures to characterize the relationship, if any, with ground water, sediment deposition, fugitive dust and other potential release migration pathways.

information on the contaminant source and the environmental setting is given in Section 13.3.

During the initial investigation particular attention should be given to sampling run-off from contaminated areas, leachate seeps and other similar sources of surface water contamination, as these are the primary release pathways for surface water.

Based on the collection and review of existing information, the design of the monitoring program is the next major step in the general approach. The monitoring program should include clear objectives, monitoring constituents and indicator parameters, monitoring locations, frequency of monitoring, and provisions for hydrologic monitoring. In addition to conventional water quality and hydrologic monitoring, sediment monitoring and biomonitoring may also have a role in the surface water evaluation for a given RFI. Guidance on the design of the monitoring program is given in Section 13.4.

Implementation of the monitoring program is the next major step in the general strategy for characterizing releases to surface water. The program should be implemented in a phased manner that allows for modifications to the program in subsequent phases. For example, initial monitoring results may indicate that downstream monitoring locations have been placed either too close to or too far from the contaminant source to accurately define the complete extent of downstream contamination. In this case, the program should be modified to relocate monitoring stations for subsequent monitoring phases. Similarly, initial monitoring may indicate that biomonitoring of aquatic organisms is needed in the next phase. Guidance on methods that can be used in the implementation of the program is given in Section 13.6.

Finally, the results of the characterization of releases to surface waters must be evaluated and presented in conformance with the requirements of the RFI. Section 13.5 provides guidance on data presentation. Table 13-2 summarizes the techniques and data-presentation methods for the key characterization tasks.

TABLE 13-2
RELEASE CHARACTERIZATION TASKS FOR SURFACE WATER

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs
1. Waste/Unit Characterization		
- Waste Composition and Analysis	- See Section 13.3.1	- Data Tables
- Unit or Facility Operations	- Review waste handling and disposal practices and schedules - Review environmental control strategies	- Schematic diagrams of flow paths, narrative
- Release Mechanisms	- See Section 13.3.1 Review operational information	- Site-specific diagrams, maps, narrative
2. Environmental Setting Characterization		
- Geographic Description	- Review topographic, soil and geologic setting information	- Maps, Tables, Narrative
- Classification of Surface Water and Receptors	- See Section 13.3.3.1	- Maps, Cross Sections, Narrative
- Define Hydrologic Factors	- See Section 13.3.3.1	- Tables, Graphs, Map
3. Release Characterization		
- Delineate Areal Extent of Contamination	- Sampling and Analysis	- Tables of Results, Contour Maps, Maps of Sampling Locations
- Define Distribution Between Sediment, Biota and Water Column	- Sampling and Analysis	- Graphs and Tables
- Determine Rate of Migration	- Flow Monitoring	- Graphs and Tables
- Describe Seasonal Effects	- Repetitive Monitoring	- Graphs and Tables

As monitoring data become available, both within and at the conclusion of discrete investigation phases, they should be reported to the regulatory agency as directed. The regulatory agency will compare the monitoring data to applicable health and environmental criteria to determine the need for (1) interim corrective measures; and (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the monitoring data with respect to adequacy and completeness to determine the need for any additional monitoring efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are supplied in Section 8. A flow diagram illustrating RFI decision points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is directed to obtain and follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

13.2.2 Inter-media Transport

Surface waters are subject to inter-media transport, both as a receptor of contamination and as a migration pathway. For example, surface waters are generally engaged in a continual dynamic relationship with ground water. Ground water may discharge to a surface water body that may, in turn, recharge an aquifer. Hence, contamination may be transported from ground water to surface water and from surface water to ground water. Release of contaminants from a receiving water body to soil can also occur through deposition of the contaminants in floodplain sediments. These sediments may be exposed to wind erosion and become distributed through fugitive dust. Sediments may be exposed to air during periods of low flow of water in streams and lakes and when sediments are deposited by overland flow during rainfall-runoff events. Contaminants may also enter the air from surface water through volatilization.

13.3 Characterization of the Contaminant Source and Environmental Setting

The initial step in developing an effective monitoring program for a release to surface waters is to investigate the unit(s) that is the subject of the RFI, the waste within the unit(s), the constituents within the waste, the operative release mechanisms and migration pathways to surface water bodies, and the surface water receptors. From this information, a conceptual model of the release can be developed for use in designing a monitoring program to characterize the release.

13.3.1 Waste Characterization

Knowledge of the general types of wastes involved is an important consideration in the development of an effective monitoring program. The chemical and physical properties of a waste and the waste constituents are major factors in determining the likelihood that a substance will be released. These waste properties may also be important initially in selecting monitoring constituents and indicator parameters. Furthermore, once the wastes are released, these properties play a major role in controlling the constituent's migration through the environment and its fate. Table 13-3 lists some of the significant properties in evaluating environmental fate and transport in a surface water system. Without data on the wastes, the investigator may have to implement a sampling program involving many constituents to ensure that all potential constituents have been addressed. General guidance on defining physical and chemical properties and identifying possible monitoring constituents and indicator parameters is provided in Sections 3 and 7.

Below are brief synopses of several of the key release, mobility, and fate parameters summarized in Table 13-3. Figure 13-1 shows the qualitative relationship between various environmental partitioning parameters. Neely and Blau (1985) provide a good description of environmental partitioning effects of constituents and application of partition coefficients.

Table 13-3

Important Waste and Constituent Properties Affecting Fate and Transport in a Surface Water Environment

Bulk waste properties affecting mobility[a]

- Physical state (solid, liquid, gas) of waste
- Chemical nature (e.g., aqueous vs non-aqueous) of waste
- Density (liquid)
- Viscosity (liquid)
- Interfacial tension (with water and minerals) (liquid)

Properties to assess mobility of constituents[b]

- Solubility
- Vapor pressure
- Henry's law constant (or vapor pressure and water solubility)
- Bioconcentration factor
- Soil adsorption coefficient
- Diffusion coefficient (in air and water)
- Acid dissociation constant
- Octanol-water partition coefficient
- Activity coefficient
- Mass transfer coefficients (and/or rate constants) for intermedia transfer
- Boiling point
- Melting point

Properties to assess persistence[c]

- Rate of biodegradation (aerobic and anaerobic)
- Rate of hydrolysis
- Rate of oxidation or reduction
- Rate of photolysis

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[a] These waste properties will be important when it is known or suspected that the waste itself has migrated into the environment, e.g., due to a spill.

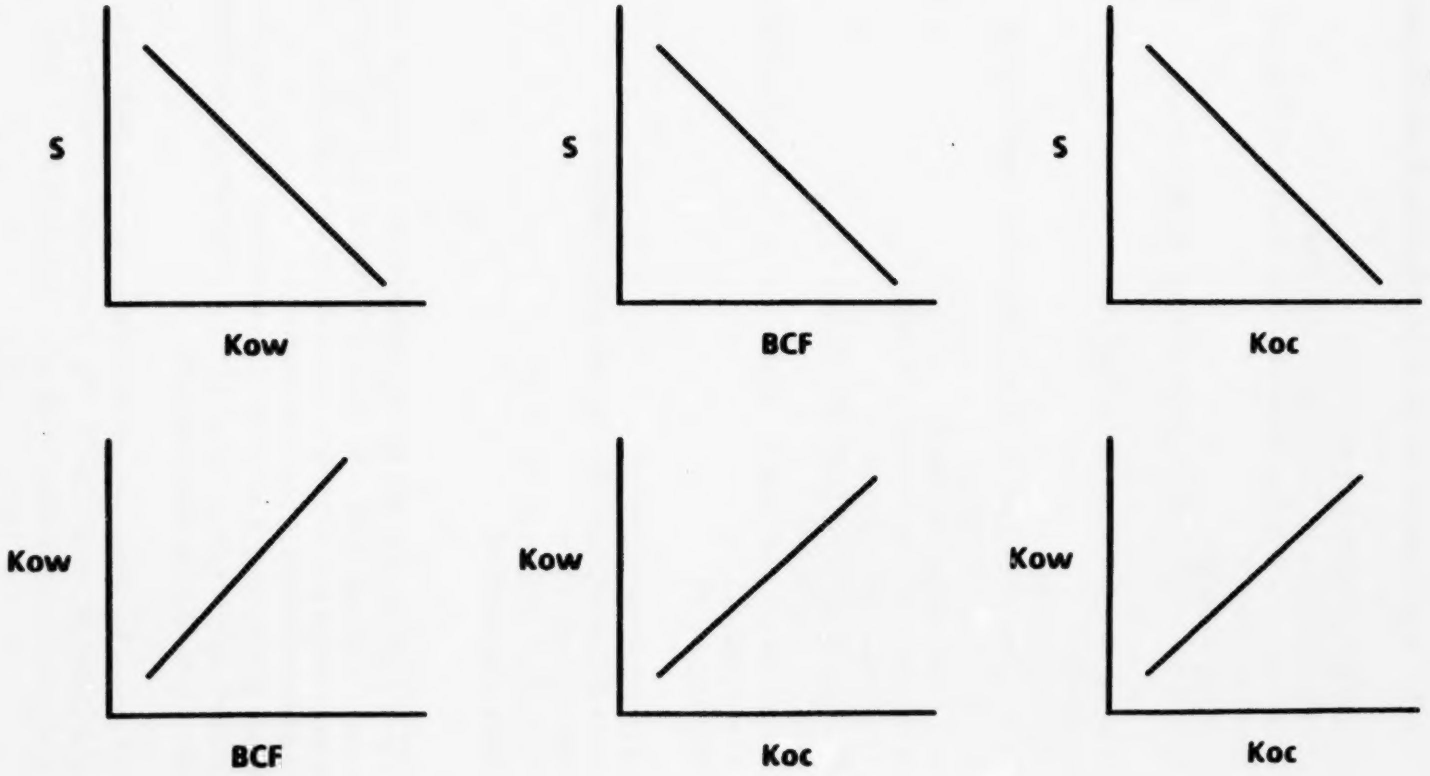
[b] These properties are important in assessing the mobility of constituents present in low concentrations in the environment.

[c] For these properties, it is generally important to know (1) the effects of key parameters on the rate constants (e.g., temperature, concentration, pH) and (2) the identity of the reaction products.

Sources of values for these and other parameters include Mabey, Smith, and Podall, (1982), and Callahan, et al. (1979). Parameter estimation methods are described by Lyman, Riehl, and Rosenblatt, (1982), and Neely and Blau (1985).

FIGURE 13-1

QUALITATIVE RELATIONSHIP BETWEEN VARIOUS PARTITIONING PARAMETERS



S: Solubility

Kow: Octanol/water partition coefficient

BCF: Bioconcentration factor

Koc: Soil/sediment adsorption coefficient

- Physical State:
  Solid wastes would appear to be less susceptible to release and migration than liquids. However, processes such as dissolution (i.e., as a result of leaching or runoff), and physical transport of waste particulates can act as significant release mechanisms.

- Water Solubility:
  Solubility is an important factor affecting a constituent's release and subsequent migration and fate in the surface water environment. Highly soluble contaminants (e.g., methanol at 4.4×10^6 mg/L at 77^oF) are easily and quickly distributed within the hydrologic cycle. These contaminants tend to have relatively low adsorption coefficients for soils and sediments and relatively low bioconcentration factors in aquatic life. An example of a less soluble constituent is tetrachloroethylene at 100 mg/L at 77^oF.

- Henry's Law Constant:
  Henry's Law Constant indicates the relative tendency of a constituent to volatilize from aqueous solution to the atmosphere based on the competition between its vapor pressure and water solubility. Contaminants with low Henry's Law Constant values (e.g., methanol, 1.10×10^{-6} atm-m^3/mole at 77^oF) will tend to favor the aqueous phase and volatilize to the atmosphere more slowly than constituents with high values (e.g., carbon tetrachloride, 2.3×10^{-2} atm-m^3/mole at 77^oF). This parameter is important in determining the potential for inter-media transport to the air media.

- Octanol/Water Partition Coefficient (K_{ow}):
  The octanol/water partition coefficient (K_{ow}) is defined as the ratio of an organic constituent's concentration in the octanol phase (organic) to its concentration in the aqueous phase in a two-phase octanol/water system. Values of K_{ow} carry no units. K_{ow} can be used to predict the magnitude of an organic constituent's tendency to partition between the aqueous and organic phases of a two phase system such as surface water and aquatic

organisms. The higher the value of K_{ow}, the greater the tendency of an organic constituent to adsorb to soil or waste matrices containing appreciable organic carbon or to accumulate in biota. Generally, constituents with K_{ow} values greater than or equal to 2.3 are considered potentially bioaccumulative (Veith et al., 1980).

- Soil-Water Partition Coefficient (K_d):
  The mobility of contaminants in soil depends not only on properties related to the physical structure of the soil, but also on the extent to which the soil material will retain, or adsorb, the hazardous constituents. The extent to which a constituent is adsorbed depends on chemical properties of the constituent and of the soil. Therefore, the sorptive capacity must be determined with reference to a particular constituent and soil pair. The soil-water partition coefficient (K_d) is generally used to quantify soil sorption. K_d is the ratio of the adsorbed contaminant concentration to the dissolved concentration, at equilibrium.

- Bioconcentration Factor (BCF):
  The bioconcentration factor is the ratio of the concentration of the constituent in an organism or whole body (e.g., a fish) or specific tissue (e.g., fat) to the concentration in water. Ranges of BCFs for various constituents and organisms are reported in the literature (Callahan, et al., 1979) and these values can be used to predict the potential for bioaccumulation, and therefore to determine whether sampling of the biota may be necessary. Constituents exhibiting a BCF greater than 1.0 are potentially bioaccumulative. Generally, constituents exhibiting a BCF greater than 100 cause the greatest concern.

- The Organic Carbon Adsorption Coefficient (K_{oc}):
  The extent to which an organic constituent partitions between the solid and solution phases of a saturated or unsaturated soil, or between runoff water and sediment, is determined by the physical and chemical properties of both the constituent and the soil (or sediment). The tendency of a constituent to be adsorbed to soil is dependent on its properties and on the organic carbon content of the soil or sediment. K_{oc} is the ratio of the

amount of constituent adsorbed per unit weight of organic carbon in the soil or sediment to the concentration of the constituent in aqueous solution at equilibrium. K_{oc} can be used to determine the partitioning of a constituent between the water column and the sediment. When constituents have a high K_{oc}, they have a tendency to partition to the soil or sediment. In such cases, sediment sampling would be appropriate.

- Other Equilibrium Constants:
  Equilibrium constants are important predictors of a compound's chemical state in solution. In general, a constituent which is dissociated (ionized) in solution will be more soluble and therefore more likely to be released to the environment and more likely to migrate in a surface water body. Many inorganic constituents, such as heavy metals and mineral acids, can occur as different ionized species depending on pH. Organic acids, such as the phenolic compounds, exhibit similar behavior. It should also be noted that ionic metallic species present in the release may have a tendency to bind to particulate matter, if present in a surface water body, and settle out to the sediment over time and distance. Metallic species also generally exhibit bioaccumulative properties. When metallic species are present in a release, both sediment and biota sampling would be appropriate.

- Biodegradation:
  Biodegradation results from the enzyme-catalyzed transformation of organic constituents, primarily from microorganisms. The ultimate fate of a constituent introduced into a surface water or other environmental system (e.g., soil), could be a constituent or compound other than the species originally released. Biodegradation potential should therefore be considered in designing monitoring programs. Section 9.3 (Soils) presents additional information on biodegradation.

- Photolysis:
  Photodegradation or photolysis of constituents dissolved in aquatic systems can also occur. Similar to biodegradation, photolysis may cause the ultimate fate of a constituent introduced into a surface water or other environmental system (e.g., soil) to be different from the constituent

originally released. Hence, photodegradation potential should also be considered in designing sampling and analysis programs.

- Chemical Degradation (Hydrolysis and Oxidation/Reduction):
  Similar to photodegradation and biodegradation, chemical degradation, primarily through hydrolysis and oxidation/reduction (REDOX) reactions, can also act to change constituent species once they are introduced to the environment. Hydrolysis of organic compounds usually results in the introduction of a hydroxyl group (-OH) into a constituent structure. Hydrated metal ions, particularly those with a valence of 3 or more, tend to form ions in aqueous solution, thereby enhancing species solubility. Mabey and Mill (1978) provide a critical review of the hydrolysis of organic compounds in water under environmental conditions. Stumm and Morgan (1982) discuss the hydrolysis of metals in aqueous systems. Oxidation may occur as a result of oxidants being formed during photochemical processes in natural waters. Similarly, in some surface water environments (primarily those with low oxygen levels) reduction of constituents may take place.

Degradation, whether biological, physical or chemical, is often reported in the literature as a half-life, which is usually measured in days. It is usually expressed as the time it takes for one half of a given quantity of a compound to be degraded. Long half-lives (e.g., greater than a month or a year) are characteristic of persistent constituents. It should be noted that actual half-life can vary significantly over reported values based on site-specific conditions. For example, the absence of certain microorganisms at a site, or the number of microorganisms, can influence the rate of biodegradation, and therefore, half-life. As such, half-life values should be used only as general indications of a chemical's persistence.

In addition to the above, reactions between constituents present in a release may also occur. The owner or operator should be aware of potential transformation processes, based on the constituents' physical, chemical and biological properties, and account for such transformations in the design of monitoring procedures and in the selection of analytical methods.

Table 13-4 provides an application of the concepts discussed above in assessing the behavior of waste material with respect to release, migration, and fate. The table gives general qualitative descriptors of the significance of some of the more important properties and environmental processes for the major classes of organic compounds likely to be encountered.

Table 13-4 can be used to illustrate several important relationships.

- Generally, water solubility varies inversely with sorption, bioconcentration, and to a lesser extent, volatilization.
- Oxidation is a significant fate process for some classes of constituents which can volatilize from the aqueous phase.
- Variations in properties and environmental processes occur within classes as indicated by the pesticides, monocyclic aromatics, polycyclic aromatics, and the nitrosamines and other nitrogen-containing compounds.

Characterizing the environmental processes and properties of inorganic waste constituents takes a similar approach to that shown on Table 13-4 for organics. However, characterizing the metals on a class-by-class basis is not advisable because of the complex nature of each metal and the many species in which the metals generally occur. The interaction of each metal species with the surface water environment is generally a function of many parameters including pH, REDOX potential, and ionic strength. See Stumm and Morgan (1982) for additional discussions on this subject. Generally, however, when metal species are present in a release, it is advisable to monitor the sediment and biota, in addition to the water column. This is due to likely deposition of metals as particulate matter, and to potential bioaccumulation.

13.3.2 Unit Characterization

The relationship between unit characteristics and migration pathways provides the framework in this section for a general discussion of release mechanisms from units of concern to surface waters.

TABLE 13-4

GENERAL SIGNIFICANCE OF PROPERTIES AND ENVIRONMENTAL PROCESSES FOR CLASSES OF ORGANIC CHEMICALS UNDER ENVIRONMENTAL CONDITIONS

Chemical Class	Solubility	Sorption	Bioconcentration	Volatilization	Photolysis	Oxidation	Hydrolysis
Pesticides							
Organochlorines	Low	High	High	High	Moderate	Low	Low
Organophosphates	Moderate	Moderate	Low	Low	High	High	Moderate-High
Carbamates	Moderate	Moderate	Moderate	Low	Moderate	Moderate	Moderate
Polychlorinated Biphenyls	Low	High	High	Moderate	Low	Low	Low
Halogenated Aliphatics	Moderate	Low	Low	High	Low	High*	Low
Halogenated Ethers	High	Low	Low	Low	Low	High*	High
Monocyclic Aromatics							
Toluene	Moderate	Moderate	Low	High	Low	High*	Low
Phenol	High	Low	Low	Low-Moderate	Moderate	Moderate	Low
Phthalate Esters	Low	High	High	Low	Low	Low	Low
Polycyclic Aromatics							
Naphthalene	Moderate	High	Low	Moderate	High**	Low	Low
Benzo(K)Fluoranthene	Low	High	Low	Low	High**	Low	Low
Nitrosamines and other Nitrogen - Containing Compounds							
Benzedine	Moderate-High	High	Low	Low	High	High	Low
Di-n-propylnitrosamine	High	Low	Low	Low	High	Low	Low

* Atmospheric oxidation (volatile organic chemicals).

** Dissolved portion only.

Table entries are qualitative only and based on a typical chemical within the class. Variations are observed within each class.

13.3.2.1 Unit Characteristics

Information on design and operating characteristics of a unit can be helpful in characterizing a release. Unsound unit design and operating practices can allow waste to migrate from a unit and possibly mix with runoff. Examples include surface impoundments with insufficient freeboard, allowing for periodic overtopping; leaking tanks or containers; or land-based units above shallow, low-permeability materials which, if not properly designed and operated, can fill with water and spill over. In addition, precipitation falling on exposed wastes can dissolve and thereby mobilize hazardous constituents. For example, at uncapped active or inactive waste piles and landfills, precipitation and leachate are likely to mix at the toe of the active face or the low point of the trench floor. Runoff may then flow into surface water through drainage pathways.

13.3.2.2 Frequency of Release

Releases to surface waters may be intermittent, continuous, or a past occurrence. It is important to consider the anticipated frequency of a release to establish an effective monitoring program.

Most of direct releases to surface waters are intermittent. Intermittent discharges may be periodic, but may occur more often in a non-periodic manner, for example, in response to rainfall runoff. Other common factors affecting intermittent releases include fluctuations in water levels and flow rates, seasonal conditions (e.g., snow melt), factors affecting mass stability (e.g., waste pile mass migration), basin configuration, quantity/quality of vegetation, engineering control practices, integrity of the unit, and process activities.

Erosion of contaminated materials from a unit (e.g., a landfill) is generally intermittent, and is generally associated with rainfall-runoff events. Similarly, breaches in a dike are generally short-term occurrences when they are quickly corrected following discovery. Leaks, while still predominantly intermittent in nature, may occur over longer spans of time and are dependent on the rate of release and the quantity of material available.

Direct placement of wastes within surface waters (e.g., due to movement of an unstable waste pile) has the potential to continuously contribute waste constituents until the wastes have been removed or the waste constituents exhausted. Direct placement is usually easily documented by physical presence of wastes within the surface water body.

The frequency of sample collection should be considered in the design of the monitoring program. For example, intermittent releases not associated with rainfall runoff may require more frequent or even continuous sample collection to obtain representative data on the receiving water body. Continuous monitoring is generally feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available. Intermittent releases that are associated with rainfall runoff may require event sample collection. With event sampling, water level or flow-activated automatic sampling/recording equipment can be used. For continuous releases, less frequent sample collection is generally adequate to obtain representative data on the receiving water body.

Previous intermittent releases may be identified through the analysis of bottom sediments, and whole body or tissue analyses of relatively sessile and long-lived macroinvertebrates (e.g., clams), or other species, such as fish. These analyses may identify constituents that may have adsorbed onto particulates and settled to the sediment, as well as bioaccumulative contaminants. In addition, intermittent releases may be detected through the use of in situ bioassays. Using these procedures, the test specie(s) is held within the effluent or stream flow and periodically checked for survival and condition.

13.3.2.3 Form of Release

Releases to surface waters may be generally categorized as point sources or non-point sources. Point sources are those that enter the receiving water at a definable location, such as piped discharges. Non-point source discharges are all other discharges, and generally cover large areas.

In general, most unit releases to surface waters are likely to be of a point source nature. Most spills, leaks, seeps, overtopping episodes, and breaches occur within an area which can be easily defined. Even erosion of contaminated soil and subsequent deposition to surface water can usually be identified in terms of point of introduction to the surface water body, through the use of information on drainage patterns, for example. However, the owner or operator should be aware of the potential for both point and non-point sources, as monitoring programs designed to characterize these types of releases can be different. For example, the generally larger and sometimes unknown areal extent of non-point source discharges may require an increase in the number of monitoring locations from that routinely required for point source discharges. The number of monitoring locations must be carefully chosen to ensure representative monitoring results.

13.3.3 Characterization of the Environmental Setting

The environmental setting includes the surface water bodies and the physical and biological environment. This section provides a general classification scheme for surface waters and discusses collection of hydrologic data that may be important in their characterization. Collection of specific geographical and climatological data are also discussed. Characterization of the biotic environment is treated in Section 13.4.

Note that some States have classified surface waters under investigations pursuant to Clean Water Act goals (e.g., Class A, B, etc.). These classifications deal primarily with the present quality of the surface water and use(s) of the surface water (e.g., drinking, recreation). If applicable, the owner or operator should report such classifications.

13.3.3.1 Characterization of Surface Waters

Surface waters can be classified into one of the following categories. These are obviously not pure classifications; intergrades are common.

- Streams and Rivers;

- Lakes and Impoundments;
- Wetlands; and
- Marine Environments.

13.3.3.1.1 Streams and Rivers

Streams and rivers are conduits of surface water flow having defined beds and banks. The physical characteristics of streams and rivers greatly influence their reaction to contaminant releases and natural purification (i.e., assimilative capacity). An understanding of the nature of these influences is important to effective planning and execution of a monitoring program. Important characteristics include depth, velocity, turbulence, slope, changes in direction and in cross sections, and the nature of the bottom.

The effects of some of these factors are so interrelated that it is difficult to assign greater or lesser importance to them. For example, slope and roughness of the channel influence depth and velocity of flow, which together control turbulence. Turbulence, in turn, affects rates of contaminant dispersion, reaeration, sedimentation, and rates of natural purification. The nature of contaminant dispersion is especially critical in the location of monitoring stations. All these factors may be of greater or lesser importance for specific sites. It should also be noted that these factors may differ at the same site depending on when the release occurred. For example, differences between winter and summer flow may greatly influence the nature of contaminant dispersion.

Of further relevance to a surface water investigation are the distinctions between ephemeral, intermittent, and perennial streams, defined as follows:

- Ephemeral streams are those that flow only in response to precipitation in the immediate watershed or in response to snow melt. The channel bottom of an ephemeral stream is always above the local water table.

- Intermittent streams are those that usually drain watersheds of at least one square mile and/or receive some of their flow from baseflow recharge from ground water during at least part of the year, but do not flow continually.

- Perennial streams flow throughout the year in response to ground water discharge and/or surface water runoff.

The distinction between ephemeral, intermittent and perennial streams will also influence the selection of monitoring frequency, monitoring locations and possibly other monitoring program design factors. For example, the frequency of monitoring for ephemeral streams, and to a lesser extent intermittent streams, will depend on rainfall runoff. For perennial-stream monitoring, the role of rainfall runoff in monitoring frequency may be of less importance under similar release situations.

The location of ephemeral and intermittent streams may not be apparent to the owner or operator during periods of little or no precipitation. Generally, intermittent and ephemeral streams may be associated with topographic depressions in which surface water runoff is conveyed to receiving waters. In addition to topography, a high density of vegetation in such areas may be an indicator of the presence of ephemeral or intermittent drainage.

Perennial streams and rivers are continually engaged in a dynamic relationship with ground water, either receiving ground water discharge (gaining stream) or recharging the ground water (losing stream) over any given stream reach. These characteristics should be considered in the evaluation of contaminant transport and fate.

The Ecology of Running Waters (Hynes 1970) and Introduction to Hydrology (Viessman et al., 1977) may be reviewed for basic discussions of surface water hydrology.

13.3.3.1.2 Lakes and Impoundments

Lakes are typically considered natural, while impoundments may be man-made. The source for lakes and impoundments may be either surface water or ground water, or both. Impoundments may be either incised into the ground surface or may be created via the placement of a dam or embankment. As with streams and rivers, the physical characteristics of lakes and impoundments influence the transport and fate of contaminant releases and therefore the design of the monitoring program. The physical characteristics that should be evaluated include dimensions (e.g., length, width, shoreline, and depth), temperature distribution, and flow pathways.

Especially in the case of larger lakes and impoundments, flow paths are not clearcut from inlet to outlet. Not only is the horizontal component of flow in question, but as depth of the water body increases in the open water zone, chemical and more commonly physical (i.e., temperature) phenomena create a vertical stratification or zonation. Figure 13-2 provides a typical lake cross section, showing the various zones of a stratified lake.

Because of stratification, deeper water bodies can be considered to be comprised of three lakes. The upper lake, or epilimnion, is characterized by good light penetration, higher levels of dissolved oxygen, greater overall mixing due to wave action, and elevated biological activity. The lower lake, or hypolimnion, is the opposite of the epilimnion. Lying between these is what has been termed the middle lake or mesolimnion, characterized by a rapid decrease in temperature with depth. Were it not for the phenomenon of lake overturn, or mixing, contaminants with specific gravities greater than water might be confined to the lowermost lake strata, where they might remain for some time. Due to the potential importance of lake mixing to contaminant transport, it is discussed below.

Temperatures within the epilimnion are relatively uniform because of the mixing that occurs there. Water is most dense at 4° Centigrade (C); above and below 4°C its density decreases. In temperate climates, lake mixing is a seasonal occurrence. As the surface of the epilimnion cools rapidly in the fall, it becomes denser than the

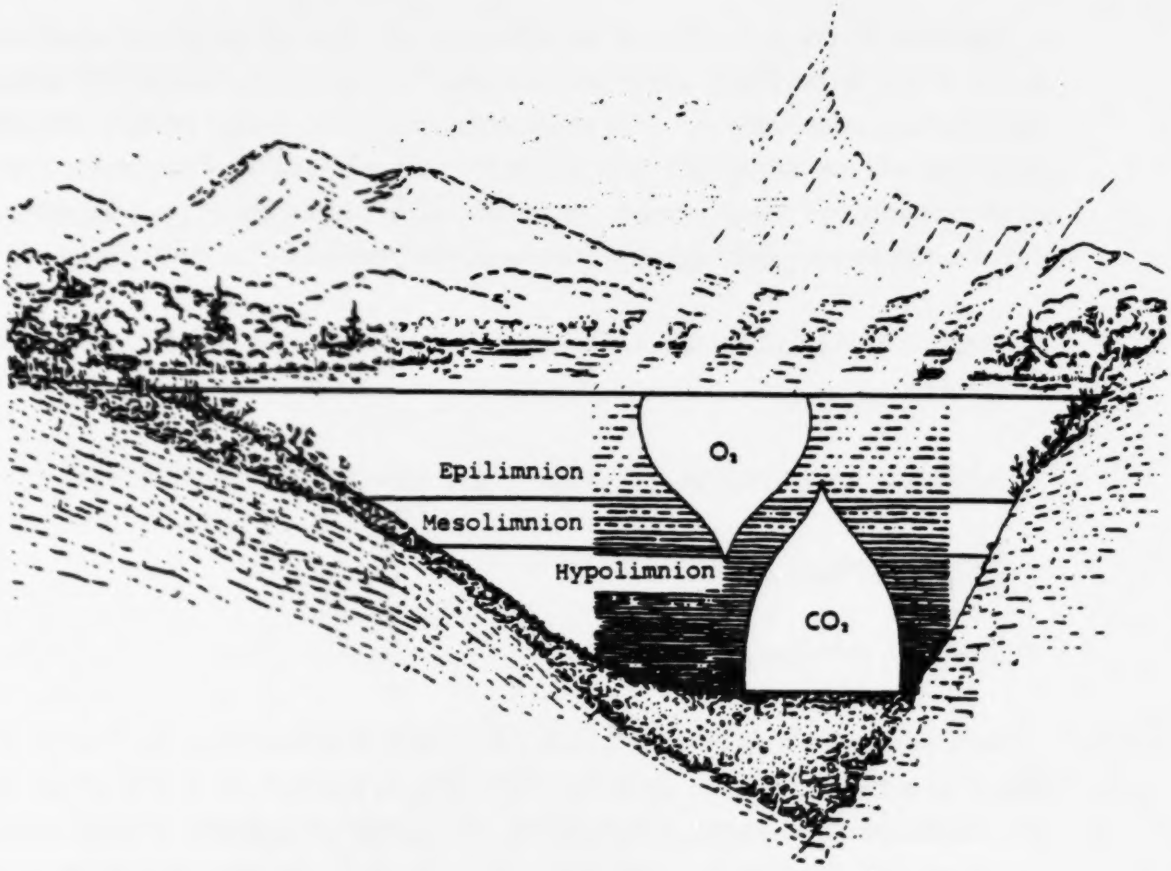

O₂
Epilimnion
Mesolimnion
Hypolimnion
CO₂

Figure 13-2. Typical Lake Cross Section (Source: Adapted From Cole, 1975).

underlying strata. At some point, the underlying strata can no longer support the denser water and an "overturn" occurs, resulting in lake mixing. A similar phenomenon occurs in the spring as the surface waters warm to 4°C and once again become denser than the underlying waters.

Because of the influence of stratification on the transport of contaminants within a lake or reservoir, the location of monitoring points will largely depend on temperature stratification. The monitoring points on water bodies that are not stratified will be more strongly influenced by horizontal flowpaths, shoreline configuration and other factors. The presence of temperature stratification can be determined by establishing temperature-depth profiles of the water body.

More information on lakes and impoundments may be found in the following references:

A Treatise on Limnology, Volumes I and II (Hutchinson, 1957, 1967) or

Textbook of Limnology (Cole, 1975)

13.3.3.1.3 Wetlands

Wetlands are those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands include, but are not limited to, swamps, marshes, bogs, and similar areas.

Wetlands are generally recognized as one of the most productive and sensitive of biological habitats, often associated with critical habitat for State or Federally listed special-status species of plants or wildlife. Wetlands also may play a significant role in basin hydrology, moderating peak surface water flows and providing recharge to the ground water system. The definition of the extent and sensitivity of wetlands that may be affected by a release is essential to release characterization.

High organic content, fine-grained sediments, slow surface water movement and lush vegetative growth and biological activity contribute to a high potential for wetlands to concentrate contaminants from releases. This is especially true for bioaccumulative contaminants, such as heavy metals. Seasonal die-off of the vegetation and flooding conditions within the basin may result in the wetlands serving as a significant secondary source of contaminants to downstream surface water receptors.

13.3.3.1.4 Marine Environments

For the purpose of this guidance, marine environments are restricted to estuaries, intermediate between freshwater and saline, and ocean environments. Industrial development near the mouths of rivers and near bays outletting directly into the ocean is relatively widespread, and the estuarine environment may be a common receptor of releases from industrial facilities.

Estuaries are influenced by both fresh water and the open ocean. They have been functionally defined as tidal habitats that are partially enclosed by land but have some access to the open sea, if only sporadically, and in which ocean water is partially diluted by fresh water. Estuaries may also experience conditions where salinities are temporarily driven above the ocean levels due to evaporative losses. Because of the protection afforded by encircling land areas, estuaries are termed "low-energy" environments, indicating that wave energy and associated erosive and mixing processes are reduced.

The physical characteristics of an estuary that will influence the design of a monitoring program are similar to those considered for lakes and impoundments (i.e., length, width, shoreline, depth, and flow pathways). However, the increased probability for chemical stratification due to varying salinities may be most pronounced in areas where freshwater streams and rivers discharge into the estuary. The monitoring program design should also consider tidal influences on stratification and contaminant dispersion.

In addition, estuaries, or some portions of estuaries, can be areas of intergrained sediment deposition. These sediments may contain a significant organic fraction, which enhances the opportunity for metal/organic adsorption, and subsequent bioaccumulation. Hence, biomonitoring within an estuary may also be appropriate.

13.3.3.2 Climatic and Geographic Conditions

A release to the surface water system will be influenced by local climatological/meteorological and geographic conditions. The release may be associated only with specific seasonal conditions like spring thaws or meteorological events such as storms. If the release is intermittent, the environmental conditions at the time of the release may help identify the cause of and evaluate the extent of the release. If the release is continuous, seasonal variations should also be evaluated.

The local climatic conditions should be reviewed to determine:

- The annual precipitation distribution (monthly averages);
- Monthly temperature variations;
- Diurnal temperature range (daytime/nighttime difference);
- Storm frequency and severity;
- Wind direction and speed; and
- Snowfall and snow pack ranges (if applicable).

This information will be useful in developing a sampling schedule and in selecting sampling methods. From these data, it should be possible to anticipate the range of climatic conditions at the site. These conditions may be far more complex than simple cold/hot or wet/dry seasons. Some areas have two or more "wet seasons", one characterized by prolonged showers, another by brief intense storms, and perhaps a third as a result of snowmelt. Cold/hot seasons may overlap these wet/dry seasons to create several climatologically identifiable seasons. Each season may affect the release differently and may require a separate characterization. The unique climatological seasons that influence the site should be identified. Typical winter, spring, summer and fall seasonal descriptions may not be appropriate or representative of the factors influencing the release. Sources of climatological data are given in Section 12 (Air).

In addition to the climatological/meteorological factors, local geographic conditions will influence the design of the sampling program. Topographic conditions and soil structure may make some areas prone to flash floods and stream velocities that are potentially damaging to sampling equipment. In other areas (e.g., the coastal dune areas of the southeastern states), virtually no runoff occurs. Soil porosity and vegetation are such that all precipitation either enters the ground water or is lost to evapotranspiration. (See Section 9 (Soil) for more information).

A description of the geographic setting will aid in developing a sampling program that is responsive to the particular conditions at the facility. When combined with a detailed understanding of the climatological/meteorological conditions in the area, a workable monitoring framework can be created.

13.3.4 Sources of Existing Information

Considerable information may already be available to assist in characterizing a release. Existing information should be reviewed to avoid duplication of previous efforts and to aid in focusing the RFI. Any information relating to releases from the unit, and to hydrogeological, meteorological, and environmental factors that could influence the persistence, transport or location of contaminants should be reviewed. This information may aid in:

- Delineating the boundaries of the sampling area;
- Choosing sampling and analytical techniques; and
- Identifying information needs for later phases of the investigation.

Information may be obtained from readily available sources of geological and meteorological data, waste characteristics, and facility operations records. (See also Sections 2, 3, 7 and Appendix A).

13.4 Design of a Monitoring Program

Following characterization of the contaminant source and environmental setting, a monitoring program is developed. This section outlines and describes factors that should be considered in design of an effective surface water monitoring program. The characterization of contaminant releases may take place in multiple phases. While the factors discussed in this section should be carefully considered in program design, each of these generic approaches may require modification for specific situations.

The primary considerations in designing a surface water monitoring program are:

- Establishing the objectives of the monitoring program;
- Determining the constituents of concern;
- Establishing the hydrologic characteristics of the receiving water and characteristics of the sediment and biota, if appropriate;
- Selecting constituents and/or indicators for monitoring;
- Selecting monitoring locations and monitoring frequency; and
- Determining the need for sediment monitoring and, hydrologic and biomonitoring.

13.4.1 Objectives of the Monitoring Program

The principal objectives of a monitoring program are to:

- Identify the characteristics of releases (e.g., continuous vs intermittent);
- Identify the fate of constituents;

- Identify the nature, rate, and extent of the release and actual or potential effects on water quality and biota; and

- Identify the effect of temporal variation on constituent fate and identify impacts on water quality and biota.

Periodic monitoring of the surface water system is often the only effective means of identifying the occurrence of releases and their specific effects. Releases can be continuous or intermittent, point source, or non-point source. The concept of monitoring is the same, regardless of the frequency or form of the release. A series of measurements, taken over time, better approximate the actual release to surface waters than a one-time grab sample.

The functional difference between monitoring the various types of discharges is the point of measurement. Point source discharges may be monitored at and/or near the discharge point to surface waters. The fate and potential effects of non-point source discharges should be inferred through measurement of the presence of constituents of concern or suitable indicators of water quality within the receiving water body.

The monitoring program should also establish the background condition against which to measure variations in a continuous release or the occurrence of an intermittent release. Such information will enable the facility owner or operator to compile data that will establish trends in releases from a given unit(s) as well as to identify releases from other sources.

Monitoring programs should characterize contaminant releases as a function of time. Climatologic factors such as frequency of intense rainfall, added effects of snowmelt, temperature extremes, and mixing in lakes and estuaries should be evaluated and quantified as causative agents for intermittent contaminant release.

Important concepts to consider in designing the monitoring program for surface water to help meet the above-stated objectives are described below.

13.4.1.1 Phased Characterization

The initial phase of a surface water release characterization program may be directed toward verification of the occurrence of a release identified as "suspected" by the regulatory agency. It may also serve as the first step for characterizing surface water systems and releases to those systems in cases where a release has already been verified.

The initial characterization will typically be a short-duration activity, done in concert with evaluation of other media that may either transport contaminants to surface waters, or may themselves be affected by discharges from surface waters (i.e., inter-media transport). It may be particularly difficult to define intermittent discharges in the initial characterization effort, especially if the contaminants from these releases are transient in the surface water body.

If the waste characterization is adequate, the initial characterization phase may rely upon monitoring constituents and suitable indicator parameters to aid in defining the nature, rate, and extent of a release. Subsequent phases of release characterization will normally take the form of an expanded environmental monitoring program and hydrologic evaluation, sensitive to seasonal variations in contaminant release and loading to the receiving water bodies, as well as to natural variation in hydrologic characteristics (e.g., flow velocity and volume, stream cross section).

13.4.1.2 Development of Conceptual Model

To effectively design a monitoring program, it is important to develop a conceptual model or understanding of the fate of constituents of the release in the receiving water body. This conceptual understanding will assist in answering the following questions.

- What portion of the receiving water body will be affected by the release and what conditions (e.g., low flow, immediate stormwater runoff) represent reasonable worst case conditions under which sampling should occur?

- What should the relative concentrations of contaminants be at specific receptor-points within the water body (e.g., public water supply intakes downstream of a site)?

- How does the release of concern relate to background contamination in the receiving water body as a result of other discharges?

- How might the monitoring program be optimized, based on contaminant dispersion and relative concentrations within the receiving water body?

The fate of waste constituents entering surface waters is highly dependent on the hydrologic characteristics of the various classifications of water bodies, (i.e., streams and rivers, lakes and impoundments, wetlands, and estuaries, as discussed earlier). Because of their complexity, methods for characterization of contaminant fate in wetlands and estuaries is not presented in detail in this guidance. The reader is referred to Mills (1985) for further detail on characterizing contaminant fate in wetlands and estuaries.

13.4.1.3 Contaminant Concentration vs Contaminant Loading

Concentration and loading are different means of expressing contaminant levels in a release or receiving water body. The concept is important in the selection of constituents for monitoring. Both concentration and loading should be evaluated with respect to the release and the receiving waters. Basing an evaluation solely on concentration may obscure the actual events. In addition, it is essential to quantify individual sources of contaminants and the relationships between media, as well as the loading found in the receiving water body, to effectively define the nature and extent of the contaminant release.

Contaminant concentrations in receiving waters have specific value in interpreting the level of health or environmental effects anticipated from the release. Contaminant loading provides a common denominator for comparison of contaminant inputs between monitoring points. In addition, especially in the case of contaminants that are persistent in sediments (e.g., heavy metals), loadings are a convenient means of expressing ongoing contributions from a specific discharge. The distinction between concentration and loading is best drawn through the following example.

A sample collected from a stream just upgradient of a site boundary (Station A) has a concentration of 50 micrograms per liter (ug/l) of chromium. A second sample collected just downstream of the site (Station B) has a chromium concentration of 45 ug/l. From these data it appears that the site is not releasing additional chromium to the stream. If, however, the stream flow is increasing between these two sampling locations, a different interpretation is apparent. If the stream flow at the upstream location is 1,000 gallons per minute (gpm) and the downstream location is 1,300 gpm, the actual loading of chromium to the stream at the two locations is as follows:

Station A

Chromium = (50.0 ug/l)(1,000 gal/min)(10^{-9} kg/ug)(60 min/hr)(3.785 l/gal) = 0.0114 kg/hr

Station B

Chromium = (45.0 ug/l)(1,300 gal/min)(10^{-9} kg/ug)(60 min/hr)(3.785 l/gal) = 0.0133 kg/hr

It is now apparent that somewhere between the two sampling stations is a source(s) contributing 0.0019 kg/hr of chromium. If all of the flow difference (i.e., 300 gpm) is from a single source, then this source would have a chromium concentration of 27.9 ug/l:

Chromium = [(0.0019 kg/hr)(10^{9} ug/kg)(1hr/60min)(1 min/300 gal)(1 gal/3.785 l)] = 27.9 ug/l

If, however, 90 percent of this flow difference (i.e., 270 gpm) was due to groundwater discharge with a chromium concentration below detectable limits and the remaining 10 percent (i.e., 30 gpm) was the result of a direct discharge from the facility, this discharge could have a chromium concentration of 279 ug/l.

13.4.1.4 Contaminant Dispersion Concepts

Contaminant dispersion concepts and models of constituent fate can be used to define constituents to be monitored and the location and frequency of monitoring. Dispersion may occur in streams, stratified lakes or reservoirs, and in estuaries. Dispersion may be continuous, seasonal, daily, or a combination of these.

The discussion below is based on information in the Draft Superfund Exposure Assessment Manual (EPA, 1986) relative to simplified models useful in surface water fate analyses. The reader is directed to that document for a more in-depth discussion of models. The equations presented below are based on the mixing zone concept originally developed for EPA's National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act. To avoid confusion over regulatory application of these concepts in the NPDES program, and the approach presented below (basically to aid in the development of a monitoring program), the following discussion refers to use of the "Dispersion Zone."

The following equation provides an approximate estimate of the concentration of a substance downstream from a point source release, after dilution in the water body:

$$C_r = \frac{C_u Q_u + C_w Q_w}{Q_u + Q_w}$$

where:

C_r = downstream concentration of substance following complete dispersion (mass/volume)
C_u = upstream concentration of substance before effluent release point (mass/volume)
C_w = concentration of substance in effluent (mass/volume)
Q_w = effluent flow rate (volume/time)
Q_u = upstream flow rate before effluent release point (volume/time)

The following equation may be used to estimate instream concentrations after dilution in situations where waste constituents are introduced via inter-media transfer or from a non-point source, or where the release rate is known in terms of mass per unit time, rather than per unit effluent volume:

$$C = \frac{T_r + M_u}{Q_t}$$

where:

T_r = inter-media transfer rate (mass/time)
M_u = upstream mass discharge rate (mass/time)
Q_t = stream flow rate after inter-media transfer or non-point source release (volume/time)

The above equations assume the following:

- Dispersion is instantaneous and complete;
- The waste constituent is conserved (i.e., all decay or removal processes are disregarded); and
- Streamflow and rate of contaminant release to the stream are constant (i.e., steady-state conditions).

For a certain area downstream of the point of release, the assumption of complete dispersion may not be valid. Under certain situations, the dispersion zone can extend downstream for a considerable distance, and concentrations can be considerably higher within the dispersion zone than those estimated by the equation. The length of this zone can be approximated by the following equation:

$$DZ = \frac{0.4\, w^2 u}{0.6\, d\sqrt{gds}}$$

where:

DZ = dispersion zone length (length units)
w = width of the water body (length units)
u = stream velocity (length/time)
d = stream depth (length units)
s = slope (gradient) of the stream channel (length/length)
g = acceleration due to gravity (32 ft/sec^2)

Within the dispersion zone, contaminant concentrations will show spatial variation. Near the release point the contaminant will be restricted (for a discharge along one shoreline) to the nearshore area and (depending on the way the discharge is introduced and its density) can be vertically confined. As the water moves downstream, the contaminant will disperse within surrounding ambient water and the plume will widen and deepen. Concentrations will generally decrease along the plume centerline and the concentration gradients away from the centerline will decrease. Eventually, as described above, the contaminant will become fully dispersed within the stream; downstream from this point concentration will be constant throughout the stream cross-section, assuming that the stream flow rate remains constant.

It is important to understand this concentration variability within the dispersion zone if measurements are to be made near the release. Relatively straightforward analytical expressions (See Neely, 1982) are available to calculate the spatial variation of concentration as a function of such parameters as stream width, depth, velocity, and dispersion coefficients. Dispersion coefficients characterize the dispersion between the stream water and contaminated influx; they can, in turn, be estimated from stream characteristics such as depth, gradient, and path (i.e., straight or bends).

The above considerations are for instream concentrations resulting from the releases of concern. If total instream concentrations are required, the concentrations determined from background water samples should also be considered. In addition, if introduction of the contaminant occurs over a fixed stream reach, as might be the case with a non-point discharge, it should be assumed that the dispersion zone begins at the furthest downstream point within this reach.

13.4.1.5 Conservative vs Non-Conservative Species

The expressions presented thus far have assumed that the contaminant(s) of concern is conservative (i.e., that the mass loading of the contaminant is affected only by the mechanical process of dilution). For contaminants that are non-conservative, the above equations would provide a conservative estimate of contaminant loading at the point of interest within the receiving water body.

In cases where the concentration after dilution of a non-conservative substance is still expected to be above a level of concern, it may be useful to estimate the distance downstream where the concentration will remain above this level and at selected points in between. The reader is referred to the Draft Superfund Exposure Assessment Manual (EPA, 1986, Section 4.3.2), for details regarding this estimation procedure.

13.4.2 Monitoring Constituents and Indicator Parameters

13.4.2.1 Hazardous Constituents

The facility owner or operator should propose a list of constituents and indicator parameters, if appropriate, to be included in the Surface Water investigation. This list should be based on a site-specific understanding of the composition of the release source(s) and the operative release mechanisms, as well as the physical and chemical characteristics of the various classes of contaminants. These factors, as well as potential release mechanisms and migration pathways, have been discussed in Sections 13.3 and 13.4.1. Also refer to Sections 3 and 7 of this guidance, and to the lists of constituents provided in Appendix B.

13.4.2.2 Indicator Parameters

Indicator parameters (e.g., chemical and biochemical oxygen demand, pH, total suspended solids, etc.) may also play a useful role in release characterization.

Though indicators can provide useful data for release verification and characterization, specific hazardous constituent concentrations should always be monitored.

Following are brief synopses of some common indicator parameters and field tests that can be used in investigations of surface water contamination. The use of biomonitoring as an indicator of contamination is discussed in Section 13.4.5.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)--BOD is an estimate of the amount of oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It may also measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Because the complete stabilization of a BOD sample may require an extended period, 5 days has been accepted as the standard incubation period. While BOD measures only biodegradable organics, non-biodegradable materials can exert a demand on the available oxygen in an aquatic environment. COD measures the total oxygen demand produced by biological and chemical oxidation of waste constituents. Availability of results for the COD in approximately 4 hours, versus 5 days for the BOD, may be an important advantage of its use in characterizing releases of a transient nature.

COD values are essentially equivalent to BOD when the oxidizable materials present consist exclusively of organic matter. COD values exceed BOD values when non-biodegradable materials that are susceptible to oxidation are present. The reverse is not often the case; however, refinery wastes provide a notable exception. There are some organic compounds, such as pulp and paper mill cellulose, that are non-biodegradable, yet oxidizable. Nitrogenous compounds, which may place a significant drain on available oxygen in aquatic environments, are not measured in the COD test. In addition, chlorides interfere with the COD test, leading to overestimates of the actual COD. BOD/COD ratios, as an indicator of biodegradability, are discussed in Section 9 (Soil). BOD and COD may be useful indicator parameters if the release is due primarily to degradable organic wastes.

Total Organic Carbon (TOC)--Total organic carbon is valuable as a rapid estimator of organic contamination in a receiving water. TOC, however, is not specific to a given contaminant or even to specific classes of organics. In addition, TOC measurements have little use if the release is primarily due to inorganic wastes.

Dissolved Oxygen (DO)--Measurements of DO may be readily made in the field with an electronic DO meter, which has virtually replaced laboratory titrations. Especially in lake environments, it is valuable to know the DO profile with depth. The bottoms of lakes are often associated with anoxic conditions (absence of oxygen) because of the lack of mixing with the surface and reduced or non-existent photosynthesis. Influx of a contaminant load with a high oxygen demand can further exacerbate oxygen deficiencies under such conditions. In addition, low DO levels favor reduction, rather than oxidation reactions, thus altering products of chemical degradation of contaminants. DO levels less than 3 mg/liter (ppm) are considered stressful to most aquatic vertebrates (e.g., fish and amphibians).

pH--pH is probably one of the most common field measurements made of surface waters. It is defined as the inverse log of the hydrogen ion concentration of an aqueous medium. pH is generally measured in the field with analog or digital electronic pH meters.

As an indicator of water pollution, pH is important for two reasons:

- The range within which most aquatic life forms are tolerant is usually quite narrow. Thus, this factor has significant implications in terms of impact to aquatic communities; and
- The pH of a solution may be a determining factor in moderating other constituent reactions.

Temperature--Along with pH, temperature is a fundamental parameter that should always be recorded in the field when a water sample is collected. Temperature is most often measured by electronic meters that can simultaneously record pH and/or specific conductance. Temperature is a significant parameter because:

- Most aquatic species are sensitive to elevated temperatures;
- Elevated temperatures can be an indication of a contaminant plume;
- Most chemical reactions are temperature-dependent; and
- Temperature defines strata in thermally-stratified lakes.

Alkalinity--Alkalinity is the capacity of water to resist a depression in pH. It is, therefore, a measure of the ability of the water to accept hydrogen ions without resulting in creation of an acid medium. Most natural waters have substantial buffering capacity (a resistance to any alteration in pH, toward either the alkaline or acid side) through dissolution of carbonate-bearing minerals, creating a carbonate/bicarbonate buffer system.

Alkalinity is usually expressed in calcium carbonate ($CaCO_3$) equivalents and is the sum of alkalinities provided by the carbonate, bicarbonate, and hydroxide ions present in solution. Alkalinities in the natural environment usually range from 45 to 200 milligrams per liter (mg/l). Some limestone streams have extremely high buffering capacities, while other natural streams are very lightly buffered and are extremely sensitive to acid (or alkaline) loadings.

Hardness--The sum of carbonate and bicarbonate alkalinities is also termed carbonate hardness. Hardness is generally considered a measure of the total concentration of calcium and magnesium ions present in solution, expressed as $CaCO_3$ equivalents.

Calcium and magnesium ions play a role in plant and animal uptake of contaminants; knowledge of the hardness of a surface water is necessary for evaluation of the site-specific bioaccumulative potential of certain contaminants (e.g., heavy metals).

Total Solids--Analytically, the total solids (TS) content of a water is that remaining after evaporation at 103-115° C or 180°C, depending on the method. The residue remaining represents a sum of the suspended, colloidal, and dissolved solids.

Hazardous constituents with high vapor pressures (i.e., volatiles, semi-volatiles) will not remain after evaporation, and will not contribute to the TS determination.

Suspended Solids--Suspended solids are those materials that will not pass a glass-fiber filter. Suspended solids contain both organic and inorganic compounds. For the purpose of comparison to water samples, the average domestic wastewater contains about 200 ppm (mg/l) of suspended solids.

Volatile Suspended Solids--Volatile suspended solids are the volatile organic portion of the suspended solids. Volatile suspended solids are the components of suspended solids that volatilize at a temperature of 600° C. The residue or ash is termed fixed suspended solids and is a measure of the inorganic fraction (i.e., mineral content). The only inorganic salt that will degrade below 600° C is magnesium carbonate.

Total Dissolved Solids--Total dissolved solids context is obtained by subtracting suspended solids from total solids. Its significance lies in the fact that it cannot be removed from a surface water or effluent stream through physical means or simple constituent processes, such as coagulation.

Salinity--The major salts contributing to salinity are sodium chloride (NaCl) and sulfates of magnesium and calcium ($MgSO_4$, $CaSO_4$). The following represents an example of classification of saline waters on the basis of salt content.

Type of Water	Total Dissolved Solids (As Salts)
brackish	1,000 to 35,000 mg/l
seawater	35,000 mg/l
brine	>35,000 mg/l

Specific Conductance--Conductivity measures the capacity to conduct current. Its counterpart is, of course, resistance, measured in ohms. The unit of conductivity has been defined as the mho. Specific conductance is conductivity/unit length. The most common units for specific conductance are mho/cm. Specific conductance can be measured instantaneously with electronic conductivity meters to comparatively high levels of accuracy and precision in the field and is an excellent real-time indicator parameter.

Conductivity generally rises with increased concentration of dissolved (ionic) species. Therefore, waters with high salinities, or high total dissolved solids, can be expected to exhibit high conductivities. Variations in specific conductance within a stream reach or a portion of an impoundment may indicate the presence of contaminant release points.

Major Ion Chemistry--The nature and prevalence of ionic species may serve as indicators of pollution from waste sources containing inorganics. Ions result from the dissociation of metal salts. The cation (e.g., Na^+, Ca^+, Mg^{++}) is typically a metallic species and the anion (e.g., Cl^-, SO_4^{--}) a non-metallic species.

A common approach to use of ion chemistry as an indicator of waste contamination in surface waters is to analyze for anions. *Standard Methods* (American Public Health Association, 1985), protocol no. 429 includes the following common anions as analytes:

Chloride (Cl^-)
Fluoride (F^-)
Bromide (Br^-)
Nitrate (NO_3^-)
Nitrite (NO_2^-)
Phosphate (PO_4^{---})
Sulfate (SO_4^{--})

While elevated concentrations of these anions may indicate the presence of inorganic constituents or other contaminants, no information will be provided regarding the identity of specific constituents or contaminants. In addition, elevated levels of anions may be associated with effluent from domestic refuse and/or runoff from fertilized agricultural fields.

The nature and concentrations of naturally-occurring ions in surface waters are a function of the geologic setting of the area, and may be temporarily affected by stormwater runoff, which may cause resuspension of streambed sediments.

In reference to their inertness with respect to constituent and biological degradation, ionic species are termed "conservative." The fact that their mass is not altered (i.e., is conserved) in surface waters permits them to be used in simple dilution modeling.

13.4.3 Selection of Monitoring Locations

The selection of monitoring locations should be addressed prior to sample acquisition because it may affect the selection of monitoring equipment and because monitoring locations will affect the representativeness of samples taken during the monitoring program. Samples must be taken at locations representative of the water body or positions of the water body with specific physical or chemical characteristics. As discussed in Section 13.4.1.2 (Development of Conceptual Model), one of the most important preliminary steps in defining monitoring locations in a surface water monitoring program is developing a conceptual model of the manner in which the release is distributed within the receiving water body. This is dependent on the physical and chemical characteristics of the receiving water, the point source or non-point source nature of the discharge, and the characteristics of the constituents themselves.

As a practical example, if a release contains contaminants whose specific gravities exceed that of water, it may behave almost as a separate phase within the receiving water body, traveling along the bottom of the water body. As another example, certain contaminants may be found in comparatively low concentrations in sediments or within the water column, yet may accumulate in aquatic biota via bioaccumulation. In this case monitoring of the biota would be advised. If the facility owner or operator is unaware of these phenomena, it would be possible for the monitoring program to show no evidence of contamination.

In general, it will be desirable to locate monitoring stations in three areas relative to the discharge in question.

- Background monitoring stations:

Background monitoring should be performed in an area known not to be influenced by the release of concern (e.g., upstream of a release).

- Monitoring stations at the release point(s) or area:

  If the release is a point source or area source, periodic monitoring should be performed at monitoring stations near the discharge origin to determine the range of contaminant concentrations. The contaminant stream (e.g., leachate seep, runoff) should also be subjected to monitoring.

- Monitoring of the receiving water body within the area of influence:

  One means of evaluating the water quality effects of a discharge is to monitor the discharge point and model its dispersion (for example using dispersion zone concepts discussed previously) within the receiving water body. The results of this modeling may be used to determine appropriate sampling locations. Actual sampling of the area thought to be influenced by the release is required. The "area of influence" may be defined as that portion of the receiving water within which the discharge would show a measurable effect. As described previously, the area to be sampled is generally defined in a phased fashion, based on a growing base of monitoring data. It is usually prudent to start with a conservatively large area and continually refine its boundaries. This is particularly true where sensitive receptors (e.g., public water supply intakes, sensitive wetlands, recreation areas) lie downstream of the release. In addition, in order to determine the full extent of the release (and its effects), samples should be taken at locations beyond the perceived area of influence.

The majority of the effort of the monitoring program will take place within the area of influence, as defined above. Many factors are involved in selecting monitoring stations within this area, the most critical being:

- The homogeneity of the water body in terms of temperature, flow, salinity, and other physical and chemical characteristics;

- The representativeness of the monitoring point, in terms of both contaminant characteristics and use factors;

- The presence of areas of pronounced water quality degradation; and

- Defensible monitoring design, including the choice of the monitoring scheme (random, stratified random, systematic, etc.), the experimental design, and adequate sample size determination.

Estuarine areas are particularly difficult in terms of selecting monitoring locations that will allow an adequate evaluation of constituent distribution, because detailed knowledge of the hydrologic characteristics of the estuary is required to accurately locate representative monitoring points. Freshwater - salt water stratification is a particularly important consideration. If stratification is known to occur or is suspected, sampling should be conducted at a range of depths within the estuary as well as at surface locations.

The selection of sampling locations is described in much greater detail in EPA (1973, 1982).

13.4.4 Monitoring Schedule

The monitoring schedule or frequency should be a function of the type of release (i.e., intermittent vs continuous), variability in water quality of the receiving water body (possibly as a result of other sources), and other factors causing the release (e.g., meteorological or process design factors). Therefore, frequency of monitoring should be determined by the facility owner or operator on a site-specific basis. All sampling points should be sampled as close to simultaneously as possible, regardless of the monitoring frequency established.

Factors important in determining the required frequency of monitoring include:

- The homogeneity of the receiving water in terms of factors that may affect the fate of constituents. The most important of these are flow and seasonal or diurnal stratification.

- The characteristics of the releases. Releases may be continuous or event-associated.

As an example, continuous, point source releases of low variability subject to few, if any, additional releases may require relatively infrequent monitoring. On the other hand, releases known to be related to recurrent causes, such as rainfall and runoff, may require monitoring associated with the event. Such monitoring is termed "event" sampling. To evaluate the threshold event required to trigger sampling, as well as the required duration of the monitoring following the event, it is necessary that the role of the event in creating a release from the unit be well understood. In what is probably the most common example, if stormwater runoff is the event of concern, a hydrograph for various storm return intervals and durations should be estimated for the point or area of interest and the magnitude and duration of its effects evaluated.

Continuous monitoring can be accomplished through in situ probes that provide frequent input to field data storage units. However, continuous monitoring is feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available.

In estuaries, samples are generally required through a tidal cycle. Two sets of samples are taken from an area on a given day, one at ebb or flood slack water and another at three hours earlier or later at half tide interval. Sampling is scheduled such that the mid-sampling time of each run coincides with the calculated occurrence of the tidal condition.

13.4.5 Hydrologic Monitoring

The monitoring program should also include provisions for hydrologic monitoring. Specifically, the program should provide for collection of data on the hydrologic condition of the surface water body at the time of sampling.

For example, some indication of the stage and discharge of a stream being monitored needs to be recorded at the time and location each water sample is collected. Similarly, for sampling that occurs during storms, a record of rainfall intensity over the duration of the storm needs to be obtained. Without this complementary hydrologic data, misinterpretation of the water quality data in terms of contaminant sources and the extent of contamination is possible.

The techniques for hydrologic monitoring that could be included in a monitoring program range in complexity from use of simple qualitative descriptions of streamflow to permanent installation of continuously-recording stream gages. The techniques appropriate in a given case will depend on the characteristics of the unit and of the surface waters being investigated. Guidance on hydrologic monitoring techniques can be found in the references cited in Section 13.6.1.

13.4.6 The Role of Biomonitoring

The effects of contaminants may be reflected in the population density, species composition and diversity, physiological condition, and metabolic rates of aquatic organisms and communities. Biomonitoring techniques can provide an effective complement to detailed chemical analyses for identifying chemical contamination of water bodies. They may be especially useful in those cases where releases involve constituents with a high propensity to bioaccumulate. This includes most metal species and organics with a high bioconcentration factor (e.g., >10) or a high octanol/water partition coefficient (e.g., ≥ 2.3). These properties were discussed in Section 13.3.

Biomonitoring techniques may include:

- Community ecology studies;
- Evaluation of food chain/sensitive species impacts; and
- Bioassays.

These techniques are discussed below.

13.4.6.1 Community Ecology Studies

Indicator species are useful for evaluating the well-being of an aquatic community that may be stressed by the release of contaminants. For example, the condition of the benthic macroinvertebrate community is commonly used as an indicator of the presence of contaminants. The objective of studying the naturally-occurring biological community is to determine community structure that would be expected, in an undisturbed habitat. If significant changes occur, perturbations in the community ecology may be linked to the disturbance associated with release of contaminants to the water body.

EPA is engaged in research to develop rapid bioassessment techniques using benthic macroinvertebrates. Although protocols are being considered, in general these techniques suffer from lack of data on undisturbed aquatic communities and associated water quality information. For some areas (e.g., fisheries), however, indices to community health based on benthic invertebrate communities are available (Hilsenhoff 1982, Cummins and Wilgbach, 1985).

Because species diversity is a commonly-used indicator of the overall health of a community, depressed community diversity may be considered an indicator of contamination. For example, if a release to surface waters has a high chemical oxygen demand (COD) and, therefore, depresses oxygen levels in the receiving water body, the number of different species of organisms that can colonize the water body may be reduced. In this case the oxygen-sensitive species (e.g., the mayfly), is lost from the community and is replaced by more tolerant species. The number of tolerant species is small, but the number of individuals within these species that can colonize the oxygen-deficient waters may be quite large. Therefore, the overall species diversity could be low, even though the numbers of organisms may be high.

Evaluations of community ecology should however, be sensitive to the role that habitat variability may play in altering community structure. Diversity of habitat may be altered by natural physical conditions (e.g., a rapid increase in stream gradient), substrate characteristics (e.g., silty versus rocky substrate), and so forth. It may also be difficult to directly link contaminant levels with the presence or absence of aquatic organisms, unless there is a secondary impact that is more self-evident, such as high oxygen demand, turbidity, or salinity.

13.4.6.2 Evaluation of Food Chain Sensitive/Species Impacts

At this level of biomonitoring, the emphasis is actually on the threat to specific fish or wildlife species, or man, as a result of bioaccumulation of constituents from the release being carried through the food web. Bioaccumulative contaminants are not rapidly eliminated by biological processes and accumulate in certain organs or body tissues. Their effect may not be felt by individual organisms that initially consume the contaminated substrate or take up the contaminants from the water. However, organisms at higher trophic levels consume the organisms of the lower trophic levels. Consequently, contaminants may become bioaccumulated in organisms and biomagnified through the food web.

Examination of the potential for bioaccumulation and biomagnification of contaminants requires at least a cursory characterization of the community to define its trophic structure, that is, which organisms occupy which relative positions within the community. Based on this definition, organisms representative of the various trophic levels may be collected, sacrificed, and analyzed to determine the levels of the contaminants of interest present.

If a specific trophic level is of concern, it may be possible to short-cut the process by selectively collecting and analyzing organisms from that level for the contaminants of concern. This may be the case, for instance, if certain organisms are taken by man either commercially or through recreational fishing, for consumption. It may also be necessary to focus on the prey of special-status fish or wildlife (e.g., eagles and other birds of prey) to establish their potential for exposure. This type of biomonitoring may be especially useful if constituents released have a relatively high potential to bioaccumulate. A discussion of indicators that are generally predictive of constituents which have a significant potential for bioaccumulation was presented in Section 13.3.

In addition, in the selection of organisms it is important to consider the ability of a given organism to accumulate a class of contaminants and the residential vs migratory nature of the organisms. For example, bullfrogs are superior for accumulating metals but poor for organics; spawning (thus migratory) salmon would be much less useful for characterizing a release from a local facility than would resident fish.

13.4.6.3 Bioassay

Bioassay may be defined as the study of specially selected representative species to determine their response to the release of concern, or to specific constituents of the release. The organisms are "monitored" for a period of time established by the bioassay method. The objective of bioassay testing is to establish a concentration-response relationship between the contaminants of concern and representative biota that can be used to evaluate the effects of the release. Bioassay testing may involve the use of indigenous organisms (U.S. EPA, 1973) or organisms available commercially for this purpose. Bioassays have an advantage over strict constituent analyses of surface waters and effluents in that they measure the total effect of all constituents within the release on aquatic organisms (within the limits of the test). Such results, therefore, are not as tightly constrained by assumptions of contaminant interactions. Discussions of bioassay procedures are provided by Peltier and Weber (1985) and Horning and Weber (1985).

The criterion commonly used to establish the endpoint for a bioassay is mortality of the test organisms, although other factors such as depressed growth rate, reproductive success, behavior alteration, and flesh tainting (in fish and shellfish) can be used. Results are commonly reported as the LC50 (i.e., the lethal concentration that resulted in 50 percent mortality of the test organisms within the time frame of the test) or the EC50 (i.e., the effective concentration that resulted in 50 percent of the test organisms having an effect other than death within the time frame of the test).

One potential use of bioassays during the RFI is to predict the effect of a release on sensitive species residing in the affected surface water(s). Bioassay may be especially useful if the release is intermittent. In this case, samples of the waste may be taken from the unit of concern and used to conduct bioassay tests. The bioassay may be conducted using the waste at 100 percent strength, and in diluted form, to obtain a concentration response relationship. The results of this testing may then be used to predict the effects of a release on the surface water biota.

Bioassays can serve as important complements to the overall monitoring program. In considering the role and design of bioassays in a monitoring program, however, the facility owner or operator should be aware of problems involved in toxicity testing. Some bioassay problems include the following considerations: toxicity meaurements are difficult to interpret in terms of actual instream impacts; toxicity test-method precision is low and difficult to quantitate; actual exposure and species sensitivity is variable; and antagonistic and synergistic effects are likely. A review of these issues is provided by Brandes et al. (1985).

13.5 Data Management and Presentation

The owner or operator will be required to report on the progress of the RFI at appropriate intervals during the investigation. The data should be reported in a clear and concise manner, and interpretations should be supported by the data. The following data presentation methods are suggested for the various phases of the surface water investigation. Further information on the various procedures is given in Section 5. Section 5 also provides guidance on various reports that may be required.

13.5.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

- Tables of waste constituents, concentrations, effluent flow and mass loadings;
- Tables of relevant physical and chemical properties of potential contaminants (e.g., solubility);
- Narrative description of unit operations;
- Surface map and plan drawings of facility, unit(s), and surface waters; and

- Identification of "reasonable worst case" contaminant release to surface waters.

13.5.2 Environmental Setting Characterization

The environment of the waste unit(s) and surface waters should be described in terms of physical and biological environments in the vicinity. This description should include:

- A map of the area portraying the location of the waste unit in relation to potential receiving waters;
- A map or narrative classification of surface waters (e.g., type of surface water, uses of the surface water, and State classification, if any);
- A description of the climatological setting as it may affect the surface hydrology or release of contaminants; and
- A narrative description of the hydrologic conditions during sampling periods.

13.5.3 Characterization of the Release

The complex nature of the data involving multiple monitoring events, monitoring locations, matrices (water, sediment, biota), and analytes lends itself to graphic presentation. The most basic presentation is a site map or series of maps that locate the monitoring stations for each monitoring event. These maps may also be adapted to include isopleths for specific analytes; however, since the isopleths imply a continuity within their borders, they may not be appropriate unless they are based on an adequate number of monitoring points and representative data. The contours should be based on unit intervals whose accuracy ranges do not overlap. In most situations, two separate reporting formats are appropriate. First, the data should be included as tables. These tables should generally be used to present the analytical results for a given sample. Each table could include samples from several locations for a given matrix, or could include samples from each location for all sample matrices. Data from these tables can then be summarized for comparison purposes using graphs.

Graphs are most useful for displaying spatial and temporal variations. Spatial variability for a given analyte can be displayed using bar graphs where the vertical axis represents concentration and the horizontal axis represents downstream distance from the discharge. The results from each monitoring station can then be presented as a concentration bar. Stacked bar graphs can be used to display these data from each matrix at a given location or for more than one analyte from each sample.

Similarly, these types of graphs can be used to demonstrate temporal variability if the horizontal axis represents time rather than distance. In this configuration, each graph will present the results of one analyte from a single monitoring location. Stacked bars can then display multiple analytes or locations. Line graphs, like isopleths, should be used cautiously because the line implies a continuity, either spatial or temporal, that may not be accurately supported by the data.

Scatter plots are useful for displaying correlations between variables. They can be used to support the validity of indicator parameters by plotting the indicator results against the results for a specific constituent.

Graphs are used to display trends and correlations. They should not be used to replace data tables, but rather to enhance the meaning of the data.

13.6 Field and Other Methods

The purpose of this section is to provide an overview of methods that can be used to characterize the nature, rate, and extent of contaminant releases to surface water. Detailed descriptions of specific methods can be found in the indicated references.

The methods presented in this section relate to four specific areas, as follows:

- Surface Water Hydrology;
- Sampling and Constituent Analysis of Surface Water, Sediments, and Biota;
- Characterization of the Condition of the Aquatic Community; and
- Bioassay Methods.

13.6.1 Surface Water Hydrology

The physical attributes of the potentially affected water body should be characterized to effectively develop a monitoring program and to interpret results. Depending on the characteristics of the release and the environmental setting, any or all of the following hydrologic measurements may need to be undertaken.

- Overland flow:
  - Hydraulic measurement;
  - Rainfall/runoff measurement;
  - Infiltration measurement; and
  - Drainage basin characterization (including topographic characteristics, soils and geology, and land use).

- Open channel flow:
  - Measurement of stage (gaging activities);
  - Measurement of width, depth, and cross-sectional area;
  - Measurement of velocity;
  - Measurement of channel discharge;
  - Measurement of channel discharge at controls (e.g., dams and weirs); and
  - Definition of flow pathways - solute dispersion studies.

- Closed conduit flow:
  - Measurement of discharge.

- Lakes and impoundments:
  - Morphometric mapping;
  - Bathymetric mapping;
  - Temperature distributions; and
  - Flow pathways.

The following references provide descriptions of the measurements described above.

National Oceanic and Atmospheric Administration. Rainfall Atlas of the U.S.

Viessman, et al., 1977. Introduction to Hydrology.

USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition Chapter 1 (Surface Water) and Chapter 7 (Physical Basin Characteristics for Hydrologic Analyses).

U.S. Department of Interior. 1981. Water Measurement Manual. Bureau of Reclamation. GPO No. 024-003-00158-9. Washington, D.C.

Chow. 1964. Open Channel Hydraulics. McGraw-Hill. New York, N.Y.

In addition, the following monographs in the Techniques of Water Resources Investigations series of the USGS (USGS-WSP-1822, 1982) give the reader more detailed information on techniques for measuring discharge and other characteristics of various water bodies and hydrologic conditions:

Benson and Dalrymple. 1967. General Field and Office Procedures for Indirect Discharge Measurement.

Bodhaine, 1968. Measurement of Peak Discharge at Culverts by Indirect Methods. USGS-TWI-03-AS.

Buchanan and Somers. 1968. Stage Measurements at Gaging Stations.

Carter and Davidian. 1968. General Procedure for Gaging Streams. USGS-TWI-03-AL.

13.6.2 Sampling of Surface Water, Runoff, Sediment, and Biota

13.6.2.1 Surface Water

The means of collecting water samples is a function of the classification of the water body, as discussed in Section 13.3.3.1. The following discussion treats lakes and impoundments separately from streams and rivers although, as indicated below, the actual sampling methods are similar in some cases. Wetlands are considered intergrade between these waters. Stormwater and snowmelt runoff is also treated as a separate category (Section 13.6.2.2). Although estuaries also represent somewhat of an intergrade, estuary sampling methods are similar to those for large rivers and lakes.

13.6.2.1.1 Streams and Rivers

These waters represent a continuum from ephemeral to intermittent to perennial. Streams and rivers may exhibit some of the same characteristics as lakes and impoundments. The degree to which they are similar is normally a function of channel configuration (e.g., depth, cross sectional area and discharge rate). Larger rivers are probably more similar to most lakes and impoundments, with respect to sampling methods, than to free-flowing headwater streams. In general, however, streams and rivers exhibit a greater degree of mixing due to their free-flowing characteristics than can be achieved in lakes and impoundments. Mixing and dilution of inflow can be slow to fast, depending on the point of discharge to the stream or river and the flow conditions.

Stream and river sampling methods do not differ appreciably from those outlined in the following section (Lakes and Impoundments). However, the selection of monitoring stations must consider additional factors created by differential flow velocities within the stream cross section. Strong currents and turbulence as a result of channel configuration may affect the amount of mixing and the distribution of contaminants in the stream. The reader may wish to refer to the references provided in Section 13.3.1 for a discussion of the manner in which differential velocities are handled in stream gaging studies to obtain representative discharge measurements.

13.6.2.1.2 Lakes and Impoundments

These waters are, by definition, areas where flow velocity is reduced, limiting the circulation of waters from sources such as discharging streams or ground water. They often include a shoreline wetland where water circulation is slow, dilution of inflowing contaminants is minimal, and sediments and plant life become significant factors in sampling strategies. The deeper zones of open water may be vertically stratified and subject to periodic turnover, especially in temperate climates. Sampling programs should be designed to obtain depth-specific information as well as to characterize seasonal variations.

Access to necessary monitoring stations may be impeded by both water depth and lush emergent or floating aquatic vegetation, requiring the use of a floating sampling platform or other means to appropriately place the sampling apparatus. It is common to employ rigid extensions of monitoring equipment to collect surface samples at distances of up to 30 or 40 feet from the shoreline. However, a boat is usually the preferred alternative for distances over about six feet. A peristaltic pump may also be used to withdraw water samples, and has the added advantage of being able to extract samples to a depth of 20 to 30 feet below the surface.

Many sampling devices are available in several materials. Samples for trace metals should not be collected in metal bottles, and samples for organics should not be collected in plastic bottles. Teflon or Teflon-coated sampling equipment, including bottles, is generally acceptable for both types of constituents. EPA (1982) and EPA (1986) provide an analysis of the advantages and disadvantages of many sampling bottles for specific sampling situations. Detailed descriptions of the use of dippers/transfer devices, pond samplers, peristaltic pumps, and Kemmerer bottles are provided by EPA (1984).

Depth-specific samples in lake environments are usually collected with equipment such as Kemmerer bottles (commonly constructed of brass), Van Dorn samplers (typically of polyvinyl chloride or PVC construction), or Nansen tubes. The depth-specific sample closure mechanism on these devices is tripped by dropping a weight (messenger) down the line. Kemmerer bottles and Nansen tubes may also be outfitted with a thermometer that records the temperature of the water at the time of collection.

13.6.2.1.3 Additional Information

Additional information regarding specific surface water sampling methods may be found in the following general references:

U.S. EPA. 1986. Methods for Evaluating Solid Wastes. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. 1984. Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods. EPA-600/4-84-076. NTIS PB-168771. Washington, D.C. 20460.

U.S. EPA. 1986. Handbook of Stream Sampling for Wasteload Allocation Applications. EPA/625/6-83/013.

U.S. EPA. 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. NTIS PB 83-124503.

USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition.

13.6.2.2 Runoff Sampling

Runoff resulting from precipitation or snowmelt creates an intermittent release situation that requires special treatment for effective sampling. The contaminant release mechanism in runoff situations may be overflow of ponds containing contaminants or erosion of contaminated soils. Based on an evaluation of the waste characteristics and the environmental setting, the facility owner or operator can determine whether waste constituents will be susceptible to this release mechanism and migration pathway.

Once it has been determined that erosion of contaminated soils is of concern, the quantity of soil transported to any point of interest, such as the receiving water body, can be determined through application of an appropriate modification of the Universal Soil Loss Equation (USLE). The USLE was developed by the U.S. Department of Agriculture, Agricultural Stabilization and Conservation Service (ASCS) to assist in the prediction of soil loss from agricultural areas. The formula is reproduced below:

$$A = RKLSCP$$

where:

A = Estimated annual average soil loss (tons/acre)
R = Rainfall intensity factor
K = Soil erodibility factor
L = Slope-length factor
S = Slope-gradient factor
C = Cropping management factor*
P = Erosion control practice factor*

*C and P factors can be assumed to equal unity in the equation if no specific crop or erosion management practices are currently being employed. Otherwise, these factors can be significantly less than unity, depending on crop or erosion control practices.

Section 3.7 (Soil Contamination) of the Draft Superfund Exposure Assessment Manual (EPA, 1986) provides a discussion of the application of the USLE to characterization of releases through soil erosion.

If the potential for significant contaminant release exists, based on analysis of the hydrologic situation and waste site characteristics, event samples should be taken during high runoff periods. In situations where high runoff is predictable, such as spring runoff or the summer thundershower season, automatic samplers may be set to sample during these periods. Perhaps the most effective way to ensure sampling during significant events is to have personnel available to collect samples at intervals throughout and following the storm. Flow data should be collected coincident with sample collection to permit calculation of contaminant loading in the runoff at various flows during the period. Automated sampling equipment is available that will collect individual samples and composite them either over time or with flow amount, with the latter being preferred. Flow-proportional samplers are usually installed with a flow-measuring device, such as a weir with a continuous head recorder. Such devices are readily available from commercial manufacturers and can be rented or leased. Many facilities with an NPDES discharge permit routinely use this equipment in compliance monitoring.

Automated samplers are discussed in Section 8 of Handbook for Sampling and Sample Preservation of Water and Wastewater (EPA, 1982) (NTIS PB 83-124503); this publication also includes other references to automated samplers and a table of devices available from various manufacturers.

13.6.2.3 Sediment

Sediment is traditionally defined as the deposited material underlying a body of water. Sediment is formed as waterborne solids (particulates) settle out of the water column and build up as bottom deposits.

Sedimentation is greatest in areas where the stream velocity decreases, such as behind dams and flow control structures, and at the inner edge of bends in stream channels. Sediments also build up where smaller, fast-flowing streams and runoff discharge into larger streams and lakes. These areas can be important investigative areas. Some sections of a streambed may be virtually without sediments. In some streams or some areas of streams, water velocity may be too fast for sediments to deposit and actually may scour the bottom, transporting material and depositing it further downstream. The stream bed in such an area will be primarily rocks and debris.

In some situations, such as low-flow conditions, the overlying water temporarily recedes, exposing sediments to the air. Runoff channels, small lakes, and small streams and rivers using may on occasion dry completely. In these cases, samples can be collected using the same procedures described in the Soils section (Section 9) of this document.

For this discussion, the definition of sediment will be expanded to include any material that may be overlain by water at any time during the year. This definition then includes what may otherwise be considered submerged soils and sludges. Submerged soils are found in wetlands and marshes. They may be located on the margins of lakes, ponds, and streams, or may be isolated features resulting from collected runoff, or may appear in areas where the ground-water table exists at or very near the land surface. In any instance they are important investigative areas.

Sludges are included for discussion here because many RCRA facilities use impoundments for treatment or storage and these impoundments generally have a sludge layer on the bottom. Sampling these sludges involves much the same equipment and techniques as would be used for sediments.

There are essentially two ways to collect sediment samples, either by coring or with grab/dredges. Corers are metal tubes with sharpened lower edges. The corer is forced vertically into the sediment. Sediments are held in the core tube by friction as the corer is carefully withdrawn; they can then be transferred to a sample container. There are many types and modifications of corers available. Some units are designed to be forced into the sediments by hand or hydraulic pressure; others are outfitted with weights and fins and are designed to free fall through the water column and are driven into the sediment by their fall-force.

Corers sample a greater thickness of sediments than do grab/dredges and can provide a profile of the sediment layers. However, they sample a relatively small surface area. Most corers are less than four inches in diameter and are more commonly two inches in diameter.

Grab/dredges are basically clamshell-type scoops that sample a larger surface area but offer less depth of penetration. Typical grab/dredge designs are the Ponar, Eckman, and Peterson versions; each has a somewhat different operating mechanism and slightly different advantages. Some use spring force to close the jaws while others are counter-levered like ice tongs.

In sediment sampling, vertical profiling is not normally required since deposition of hazardous material is often a recent activity in terms of sedimentary processes. Grab/dredges that sample a greater surface area may be more appropriate than corers. Similarly, shallow sludge layers contained in surface impoundments should be sampled with grab/dredges because corer penetration could damage the impoundment liner, if present. Thicker sludge layers which may be present in surface impoundments, may be sampled using coring equipment if it is important to obtain vertical profile information.

Submerged soils are generally easier to sample with a corer, than with a grab/dredge because vegetation and roots can prevent the grab/dredges from sealing completely. Under these conditions, most of the sample may wash out of the device as it is recovered. Corers can often be forced through the vegetation and roots to provide a sample. In shallow water, which may overlie submerged soils, sampling personnel can wade through the water (using proper equipment and precautions) and choose sample locations in the small, clear areas between vegetative stems and roots.

A wide variety of sampling devices are available for collection of sediment samples. Each has advantages and disadvantages in a given situation, and a variety of manufacturers produce different versions of the same device. As with water sampling, it is important to remember that metal samplers should not be used when collecting samples for trace metal analysis, and sampling devices with plastic components should not be used when collecting samples for analysis of organics.

The following references describe the availability and field use of sediment samplers:

U.S. EPA. 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. Environmental Monitoring and Support Laboratory, EPA-600/4-82-029. NTIS PB 83-124503.

U.S. EPA. 1985. Methods Manual for Bottom Sediment Sample Collection. NTIS PB 86-107414.

USGS. 1977, update June 1983. National Handbook of Recommended Methods for Water-Data Acquisition.

U.S. EPA. 1984. Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods. EPA-600/4-84-076. NTIS PB 85-168771.

13.6.2.4 Biota

Collection of biota for constituent analysis (whole body or tissue) may be necessary to evaluate exposure of aquatic organisms or man to bioaccumulative contaminants. For the most part, collection should be restricted to representative fish species and sessile macroinvertebrates, such as mollusks. Mollusks are filter-feeders; bioaccumulative contaminants in the water column will be extracted and concentrated in their tissues. Fish species may be selected on the basis of their commercial or recreational value, and their resultant probability of being consumed by man or by special status-species of fish or wildlife.

The literature on sampling aquatic organisms is large. Most sampling methods include capture techniques that be collected using sampling bottles (as for water samples) or nets of appropriate mesh sizes. Periphyton may be most easily collected by scraping off the substrate to which the organisms are attached. Other techniques using artificial substrates are available if a quantitative approach is required. Aquatic macroinvertebrates may be collected using a wide variety of methods, depending on the area being sampled; collection by hand or using forceps may be efficient. Grab sampling, sieving devices, artificial substrates and drift nets may also be used effectively. EPA (1973) provides a discussion of these techniques, as well as a method comparison and description of data analysis techniques.

Fish collection techniques may be characterized generally as follows (USGS, 1977):

- Entangling gear:
  Gill nets and trammel nets.
- Entrapping gear:
  Hoop nets, basket traps, trap nets, and fyke and wing nets.
- Encircling gear:
  Haul seine, purse seine, bay seine, and Danish seine.
- Electroshocking gear:
  Boat shockers, backpack shockers, and electric seines.

Selection of sampling equipment is dependent on the characteristics of the water body, such as size and conditions, the size of the fish to be collected, and the overall objectives of the study. Fisheries Techniques (Nielsen and Johnson, 1983) and Guidelines for Sampling Fish in Inland Waters (Backiel and Welcomme, 1980) provide basic descriptions of sampling methods and data interpretation from fisheries studies.

13.6.3 Characterization of the Condition of the Aquatic Community

Evaluation of the condition of aquatic communities may proceed from two directions. The first consists of examining the structure of the lower trophic levels as an indication of the overall health of the aquatic ecosystem. With respect to RFI studies, a healthy water body would be one whose trophic structure indicates that it is not impacted by contaminants. The second approach focuses on a particular group or species, possibly because of its commercial or recreational importance or because a substantial historic data base already exists.

The first approach emphasizes the base of the aquatic food chain, and may involve studies of plankton (microscopic flora and fauna), periphyton (including bacteria, yeast, molds, algae, and protozoa), macrophyton (aquatic plants), and benthic macroinvertebrates (e.g., insects, annelid worms, mollusks, flatworms, roundworms, and crustaceans). These lower levels of the aquatic community are studied to determine whether they exhibit any evidence of stress. If the community appears to have been disturbed, the objective is to characterize the source(s) of the stress and, specifically, to focus on the degree to which the release of waste constituents has caused the disturbance or possibly exacerbated an existing problem. An example of the latter would be the further depletion of already low dissolved oxygen levels in the hypolimnion of a lake or impoundment through the introduction of waste with a high COD and specific gravity.

The sampling methods referenced in Section 13.6.2.4 may be adapted (by using them in a quantitative sampling scheme) to collect the data necessary to characterize aquatic communities. Hynes (1970) and Hutchinson (1967) provide an overview of the ecological structure of aquatic communities.

Benthic macroinvertebrates are commonly used in studies of aquatic communities. These organisms usually occupy a position near the base of the food chain. Just as importantly, however, their range within the aquatic environment is restricted, so that their community structure may be referenced to a particular stream reach or portion of lake substrate. By comparison, fish are generally mobile within the aquatic environment, and evidence of stress or contaminant load may not be amenable to interpretation with reference to specific releases.

The presence or absence of particular benthic macroinvertebrate species, sometimes referred to as "indicator species," may provide evidence of a response to environmental stress. Several references are available in this regard. For more information, the reader may consult Selected Bibliography on the Toxicology of the Benthic Invertebrates and Periphyton (EPA, 1984).

A "species diversity index" provides a quantitative measure of the degree of stress within the aquatic community, and is an example of a common basis for interpretation of the results of studies of aquatic biological communities. The following equation (the Sannon-Wiener Index) demonstrates the concept of the diversity index:

$$H = \sum_{i=1}^{s} (Pi)(\log_2 Pi)$$

where:

H = species diversity index

s = number of species

pi = proportion of total sample belonging to the ith species

Measures of species diversity are most useful for comparison of streams with similar hydrologic characteristics or for the analysis of trends over time within a single stream. Additional detail regarding the application of other measures of community structure may be found in the following references:

U.S. EPA. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Water and Effluents.

USGS. 1977, Update May, 1983. National Handbook of Recommended Methods of Water-Data Acquisition.

Curns, J. Jr., and K.L. Dickson, eds. 1973. ASTM STP 528: Biological Methods for the Assessment of Water Quality. American Society for Testing and Materials. STP528. Philadelphia, PA.

The second approach to evaluating the condition of an aquatic community is through selective sampling of specific organisms, most commonly fish, and evaluation of standard "condition factors" (e.g., length, weight, girth). In many cases, receiving water bodies are recreational fisheries, monitored by state or federal agencies. In such cases, it is common to find some historical record of the condition of the fish population, and it may be possible to correlate operational records at the waste management facility with alterations in the status of the fish population.

Sampling of fish populations to evaluate condition factors employs the same methodologies referenced in Section 13.6.2.4. Because of the intensity of the effort usually associated with obtaining a representative sample of fish, it is common to coordinate tissue sampling for constituent analysis with fishery surveys.

13.6.4 Bioassay Methods

The purpose of a bioassay, as discussed is more detail in Section 13.4.6.3, is to predict the response of aquatic organisms to specific changes within the environment. In the RFI context, a bioassay may be used to predict the potential adverse environmental effects of releases to surface water. Thus, bioassay is not generally considered to be an environmental characterization or monitoring technique. As indicated below, bioassay may be required for Federal water quality programs or state programs, especially where stream classification (i.e., warm-water fishery, cold-water fishery) is involved.

Bioassays may be conducted on any aquatic organism including algae, periphyton, macroinvertebrates, or fish. Bioassay includes two main techniques, acute toxicity tests and chronic toxicity tests. Each of these may be done in a laboratory setting or using a mobile field laboratory. Following is a brief discussion of acute and chronic bioassay tests.

Acute Toxicity Tests--Acute toxicity tests are used in the NPDES Permit Program to identify effluents containing toxic wastes discharged in toxic amounts. The data are used to predict potential acute and chronic toxicity in the receiving water, based on the LC50 and appropriate dilution, and application of persistence factors. Two types of tests are used; static and flow-through. The selection of the test type will depend on the objectives of the test, the available resources, the requirements of the test organisms, and effluent characteristics. Special environmental requirements of some organisms may preclude static testing.

It should be noted that a negative result from an acute toxicity test with a given effluent sample does not preclude the presence of chronic toxicity, nor does it negate the possibility that the effluent may be acutely toxic under different conditions, such as variations in temperature or contaminant loadings.

There are many sources of information relative to the performance of acute bioassays. Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Peltier and Weber, 1985) provides a comprehensive treatment of the subject.

Chronic Toxicity Tests--Chronic toxicity tests may include measurement of effluent effects on growth and reproductive success. These tests usually require long periods of time, depending on the life cycles of the test organisms. Chronic bioassays are generally relatively sophisticated procedures and are more intensive in terms of manpower, time and expense than are acute toxicity tests. The inherent complexity of these tests dictate careful planning with the regulatory agency prior to initiation of the work. Methods for Measuring the Chronic Toxicity of Effluents to Aquatic Organisms (Horning and Weber, 1985) is a companion volume to the methods document noted above, and contains method references for chronic toxicity tests. A discussion of bioassay procedures is also provided in Protocol for Bioassessment of Hazardous Waste Sites, NTIS PB 83-241737. (Tetra Tech, 1983).

13.7 Checklist

RFI Checklist - Surface Water

Site Name/Location ______________________

Type of Unit ______________________

1. Does waste characterization include the following information? (Y/N)

• Constituents of concern	______
• Concentrations of constituents	______
• Mass of the constituent	______
• Physical state of waste (e.g., solid, liquid, gas)	______
• Water solubility	______
• Henry's Law Constant	______
• Octanol/Water Partition Coefficient (K_{ow})	______
• Bioconcentration Factor (BCF)	______
• Adsorption Coefficient (KOC)	______
• Physical, biological, and chemical degradation	______

2. Does unit characterization include the following information? (Y/N)

• Age of unit	______
• Type of unit	______
• Operating practices	______
• Quantities of waste handled	______
• Presence of cover or other surface covering	______
• Dimensions of unit	______
• Presence of natural or engineered barriers near unit	______
• Release frequency	______
• Release volume and rate	______
• Non-point or point source release	______
• Intermittent or continuous release	______

3. Does environmental setting information include the following?

(Y/N)

- Areal extent of drainage basin ________
- Location and interconnection of all streams, lakes and other features ________
- Flow identification as ephemeral, intermittent or perennial ________
- Channel alignment, gradient and discharge rate ________
- Flood and channel control structures ________
- Source of lake and impoundment water ________
- Lake and impoundment depths and surface area ________
- Vertical temperature stratification of lakes and impoundments ________
- Wetland presence and role in basin hydrology ________
- NPDES and other discharges ________
- USGS gaging stations or other existing flow monitoring systems ________
- Surface water quality characteristics ________
- Average monthly and annual precipitation values ________
- Average monthly temperature ________
- Average monthly evaporation potential estimates ________
- Storm frequency and severity ________
- Snowfall and snow pack ranges ________

4. Have the following data on the initial phase of the release characterization been collected? (Y/N)

- Monitoring locations ________
- Monitoring constituents and indicator parameters ________
- Monitoring frequency ________
- Monitoring equipment and procedures ________
- Concentrations of constituents and locations at which they were detected ________
- Background monitoring results ________

- Hydrologic and biomonitoring results ______
- Inter-media transfer data ______
- Analyses of rate and extent of contamination ______

5. Have the following data on the subsequent phase(s) of the release characterization been collected? (Y/N)
   - New or relocated monitoring locations ______
   - Constituents and indicators added or deleted for monitoring ______
   - Modifications to monitoring frequency, equipment or procedures ______
   - Concentrations of constituents and locations at which they were detected ______
   - Background monitoring results ______
   - Hydrologic and biomonitoring results ______
   - Inter-media transfer data ______
   - Analyses of rate and extent of contamination ______

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APPENDIX E

THE EMISSION ISOLATION FLUX CHAMBER

APPENDIX E

- THE EMISSION ISOLATION FLUX CHAMBER

GENERAL DESCRIPTION

The Emission Isolation Flux Chamber technique is a direct approach that uses an enclosure device (flux chamber) to sample gaseous emissions from a defined surface area. Clean, dry sweep air is added to the chamber at a fixed controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is expressed as:

$$E_i = C_i R/A \qquad \text{(Equation 1)}$$

where, E_i = emission rate of component i, lb/ft^2-sec

C_i = concentration of component i in the air flowing from the chamber, lb/ft^3

R = flow rate of air through the chamber, ft^3/sec

A = surface area enclosed by the chamber, ft^2

All parameters in Equation 1 are measured directly. The general reference for use of this device is:

> U.S. EPA, 1986. Measurement of Gaseous Emissions Rates from Land Surfaces Using an Emissions Isolation Flux Chamber: Users Guide. EPA 600/8-86-008. NTIS PB 86-223161. Washington, D.C. 20460.

A diagram of the flux chamber apparatus is shown in Figure E-1. The sampling equipment consists of a stainless steel/acrylic chamber with impeller, ultra-high purity sweep air and rotameter for measuring flow into the chamber, and a sampling manifold for monitoring and/or collection of the specie(s) of interest.

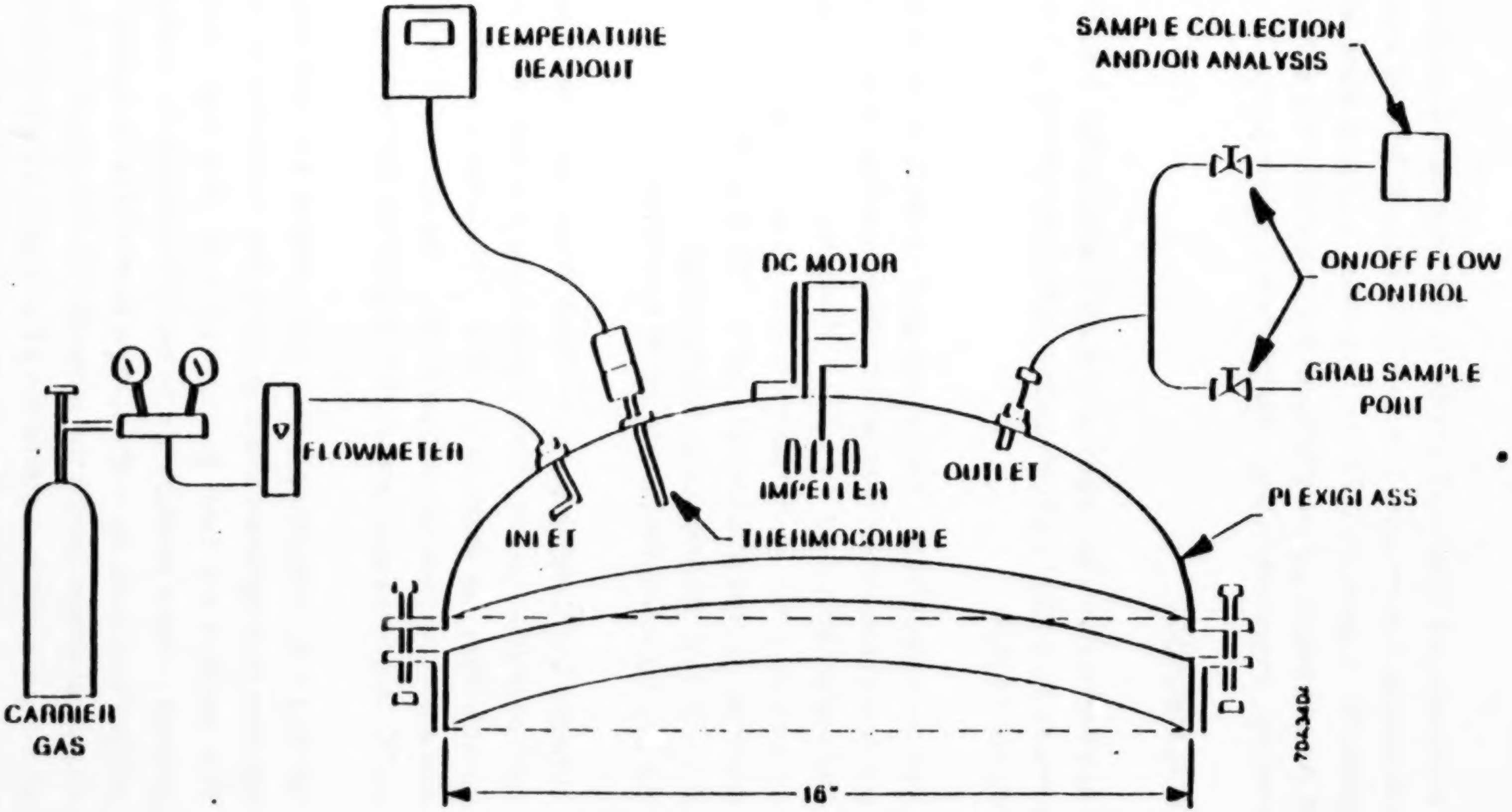
TEMPERATURE READOUT
SAMPLE COLLECTION AND/OR ANALYSIS
DC MOTOR
ON/OFF FLOW CONTROL
GRAB SAMPLE POINT
FLOWMETER
OUTLET
IMPELLER
PLEXIGLASS
INLET
THERMOCOUPLE
CARRIER GAS
16"

Figure E-1. Surface Flux Chamber and Peripheral Equipment

Concentrations of total hydrocarbons are monitored continuously in the chamber outlet gas stream using portable FID- and/or PID-based analyzers. Samples are collected for subsequent GC analysis once a steady-state emission rate is obtained. Air and soil/liquid temperatures are measured using a thermocouple. The system pressure is monitored using a Magnahelic pressure gauge.

ANALYTICAL METHODS

The analytical systems generally used during surface flux chamber sampling are real-time monitors, portable gas chromatographs, and off-site gas chromatographs. Each is described below.

- Real-time monitors - These are used to determine when steady-state conditions have been reached and when syringe sampling can be initiated. The instruments used are a PID with a range of 0.1-2000 ppmv and an FID with a range of 1-10,000 ppmv. Generally speaking, the PID shows a better response to aromatic species and the FID to aliphatic species. Based upon the real-time monitor data, the sweep air flow rate is adjusted to achieve the desired concentration range for GC analysis.

- Portable Gas Chromatograph - Once steady state had been reached and verified in the flux chambers, a grab sample is collected in a glass gas- tight syringe from the chamber exit line. The samples are shielded from light and analyzed generally within 30 min. The GC used is equipped with a PID or FID. A packed capillary column is operated isothermally.

- Off-Site Gas Chromatograph - Gas samples are collected in evacuated stainless steel canisters and shipped to the laboratory for detailed analysis. The canisters are then pressurized with ultra high purity nitrogen to provide positive pressure for removing the sample for analysis and to dilute oxygen and moisture in the sample to minimize component reactions. The analytical system used is the same GC/FID, PID system. If necessary, aliquots of the gas canister samples can be analyzed by gas chromatography/mass spectrometry (GC/MS) to verify the species identifications.

METHOD EVALUATION

Some of the advantages of the flux chamber technique include:

- The soil and any associated emission processes are undisturbed;
- Sampling is rapid, normally requiring 1/2 hr per sampling point;
- The technique is suited to most soil types;
- The sampling equipment used is fairly simple and widely available; and
- The sampling technique's accuracy and precision is well documented.

Disadvantages of the flux chamber technique include:

- The sweep air dilutes the gas sample and therefore decreases the method's sensitivity;
- The flux chamber sampling technique has a measurable effect on the emission rate being measured;
- Gas concentrations at the surface are normally lower than at subsurface sampling locations;
- The technique functions poorly when the soil being sampled is saturated with water and gas transport pathways are blocked; and
- Sites with caliche or other semi-impermeable soil strata may be unsuited for sampling by this method.